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2012 **NOLWAZI SANELISIWE NGCOBO**

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ELECTROSPUN CARBON NANOPARTICLES/ POLYMERS COMPOSITE NANOFIBERS

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Abstract

Polymer Nanocomposites have existed for decades now with different type of additives present in the polymer. The effect of properties depends on the scale of fillers. Nanofillers have increased within the years from nanoclays to carbon nanoparticles as well as the matrix in which they are used. The development of polymer nanocomposites is becoming more active in the area of nanomaterial because of their unique properties including optical, electrical, mechanical, thermal as well as fire retardant properties. These properties strongly depend on the mixing ratio between the organic matrix and nanofillers.

Fullerenes have shown interest in the field of research due to unique chemical and physical properties that have been utilized in different fields of application in nanotechnology. The core was to focus on the mass weight of buckyballs fullerene C60 properties in polyurethane (PUR) and polyvinyl alcohol (PVA) polymer matrices to form stable polymer nanocomposites by using needleless electrospinning Nanospider™ technology and rod electrospinning that would be applicable for flame retardancy material and anti-micro bacterial materials.

The presence of fullerenes in polymers was investigated by thermogravimetric analysis (TGA), scanning electron microscope (SEM), Energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. TGA results showed that the presence of C60 could enhance the thermal stability of organic polymers since organic polymers are inherently flammable. The larger the C60 level present, the better the flame retardancy of nanocomposites. Fullerenes are becoming good candidate as highly effective flame retardancy for polymeric materials by enhancing the flame retardancy properties.

Keywords

Nanocomposites, fullerene C60, rod electrospinning, nanospider™, thermal stability, flame retardancy

Preface

This work was carried out in the Department of Nonwoven Textile at Technical University of Liberec from 2011-2012. The reported results were obtained from Nonwoven Laboratories as well as outside from the university due to Textile building construction, from the TGA Laboratory in Prague and Raman and EDS Laboratories in Budapest University of Technology and Economics.

I would like to thank all people who attributed to my project and for the academic support that I have received during my studies at Technical University of Liberec from 2010-2012. I will special thank my supervisor Ing. Bc. Eva Košťáková, Katedra netkaných textilií, who has been the greatest key behind my development as a researcher and for the guidance in order to finish this research project.

I would also like to thank the laboratory assistant Ing. Denisa Zálešáková for preparation of all the solutions and setting of sonication ultrasound machine and the technicians Filip Sanetrník for the setting and running of cylinder electrospinning machine.

I would also like to thank people from Prague doc. Karel Klouda and Ing. Eva Zemanová and Dr. Meszaros Laszlo (SEM-EDS), Dr. Zsombor K. Nagy (Raman spectroscopy) - both Budapest University of Technology and Economics for devoting their time and try to help out and do some analysis while our textile building was still under construction.

My last thank you goes t o Department of Textile in TUL and department of Economic Development in KZN for giving me this great oppoortunity to do my studies at TUL that has groomed me as a researcher. To Ing. Hana Musilová, Dr. Rajesh Mishra and my family thank you for being there all the time within my 2 years in Czech Republic.

List of Symbols and Abbreviations

d	Diameter
C	Concentration
η	Viscosity
α	Alpha scaling exponent
β	Beta scaling exponent
δ	Delta scaling exponent
PUR	Polyurethane
PVA	Poly (vinyl alcohol)
PVB	Poly (vinyl butharate)
DMF	Dimethylformamide
TEAB	Tetraethylammoniumbromide
CNT	Carbon nanotube
SWNT	Single walled nanotube
MWNT	Multi walled nanotubes
LOI	Limiting Oxygen Index
RH	Relative humidity
EDS	Energy-Dispersive X-ray Spectroscopy
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis

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1. Introduction

Composites are materials made up of two or more of individual materials referred to as constituent materials with significantly different physical or chemical properties which remain separate and distinct on a microscopic level within the finished structure and they do not dissolve or blend into each other. The matrix material surrounds and supports the reinforcement material by maintaining their relative positions. The reinforcing material improves mechanical and physical properties to enhance the matrix properties. Composites are able to stand up well to heat and corrosion. They are durable and flexible.

Polymer composites are most used in textile industry for variety applications because of their mechanical properties, i.e. low strength and modulus for polymers combined with high tensile strength and modulus fillers (fibers, particles) to make composites [1]. These fillers normally have micro-/nano-scales and may act as stress concentration sites leading to embitterment of polymer [2, 3]. There are two types of polymers that are used including thermoplastics and thermosets

Nanocomposites are of significantly interest in the industry because of their extremely small size fillers that leads to unique properties and also unprecedented morphologies of the composites. Polymer nanocomposites are materials in which the filler phase is dispersed in the polymer matrix at a nanoscale and at least one dimension of the filler is less than 100 nm The nanoscale dispersion of the filler leads to tremendous interfacial contact between the phases and completely change the morphology of the composite from that of convectional microcomposites where the mix is at macroscale. This allows polymer performance to be enhanced at lower filler volume fraction whereby the polymer retains its transparency [4].

Nanocomposites differ from conventional composites because of exceptional high surface area to volume ratio and aspect ratio of the reinforcing phase. The interface of matrix and reinforcement is greater than of conventional composites by an order of magnitude. Polymer nanocomposites have their properties related to local chemistry, degree of thermoset cure and of polymer chain ordering, polymer chain mobility and conformation significantly varying continuously from the interface with the reinforcement and the matrix.

Certain percentage of nanofillers that can be added and create a huge amount of filler-polymer interface and a polymer matrix is then considered as nano-scopically confined interfacial polymer because of the imperfect bonding of carbon nanotubes and polymer matrix. Nanofillers then are able to restrict the conformation of polymer chain and mobility leading to a change of relaxation behavior and thermal transitions. Nanofillers can also influence the degree of ordering and crystal packing of semicrystalline poly (vinyl alcohol) therefore the crystallinity of polymer is altered [5].

Fullerenes have become attraction in research fields due to unique chemical and physical properties that have been utilized in different application fields in nanotechnology [6]. The C60 fullerene has become available in multigram amounts with the preparation procedure of Krätschmer and Huffman [7]. Fullerenes have been proposed as an ideal molecules to serve some purposes by reacting with different polymers (PUR and PVA) using both rod and cylinder needlessless electrospinning. The study of this kind of information has been discussed by including SEM, EDS, Raman Spectroscopy and TGA analysis in order to determine fullerenes effect in polymer solutions.

Convectional electrospinning has been in industries for some years now but despite the potential enormous applications still meets difficulties in broad applications in practice. This is because of the lack of economic and efficient way to scale up the electrospinning process [8]. The multi-needle electrospinning took over syringe electrospinning but has disadvantage of solution blockage during fiber production so needleless become an alternative way. Needless electrospinning showed high ability to produce nanofibers in large scales by forming enormous jets simultaneously without the influence of capillary effect. Needle electrospinning has typical low production rate of 0.3g/hr compared to needleless electrospinning with high production rate although it is a self-organized process and hard to control [8].

1.1. Objectives and Approach

The aim of this thesis was to apply the method of electrospinning in order to manufacture material of different applications including flame retardancy with regards to selected polymers including PVA and PUR. These materials have to be produced from nanostructured fiber composites suitable for required applications.

There are two types of electrospinning methods utilized in this thesis for the preparation of nanofiber composites (nanocomposites) with various compositions. Different types of properties are examined for the suitable use in required applications. Rod and Cylinder electrospinning techniques were used. Rod electrospinning is conducted using free liquid surface from the top of the rod and cylinder from rotational cylinder immersed in the solution.

The purpose of this thesis is to obtain materials suitable for flame/fire retardancy (fire resistivity) from different needless electrospinning technologies.

1.2. Related work done previously

Fullerene C60 and its derivatives as nanocomposites in polymer nanofibers have been researched before by Eva Kostakova, Eva Zemarova and karel Klouda at Technical University of Liberec. The nanocomposites polymer nanofibers 1 wt% of C60oxi was produced by needleless electrospinning using different solutions in different solvents and distilled water. The polymers used were poly (vinyl alcohol) PVA (10wt %) in water, polyurethane PUR (10wt %) in DMF and poly (vinyl butharate) PVB (10wt %) in acetic acid and methanol. F. Cengiz and O. Jirsak have also focus on the spinnability of polyurethane nanofibers with roller electrospinning (nanospider) investigating the effect of salt TEAB in the polyurethane solutions.

2. Electrospinning Methods

Electrospinning is a spinning technique from polymer solution using electrostatic force to form fibers and it utilizes high voltage electric field to produce jet of polymer fluid. An electrode charges the polymer fluid which ejects into a fine fluid jet. Then the fluid jet splits and elongates as it accelerates under the electric field. The solvent from the jet evaporates rapidly due to its large surface area and solidifies and produces nanofibers which are deposited isotropic in a form of a web [9]. There are various ways of producing nanofibers, i.e. drawing technology that uses a micropipette to produce microfibers or nanofibers and electrospinning which is the cheapest and easy to use. Electrospinning started in 1934 by Formahals (figure 1) where polymer filaments were produced using electrostatic force. Electrospinning process protruded from electrostatic spraying [10].

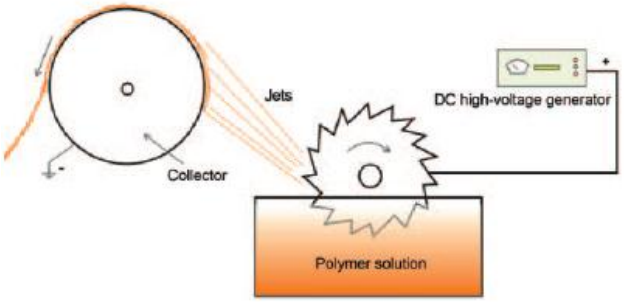


Figure 1: Formahals' electrospinning set up [10]

Electrospinning is a novel process for producing superfine fibers by forcing a viscous polymer, composite, sol-gel solution or melt through a spinneret with an electric field to a droplet of the solution, most often at a metallic needle tip [10].

The use of electric field is to draw this droplet into a structure called a Taylor cone (figure 2) [9]. The electrospray then will occur when varicose breaks up but this could be avoided if the surface tension and viscosity of the solution is appropriately tuned [10]. There are two type's needle and needless electrospinning processes.

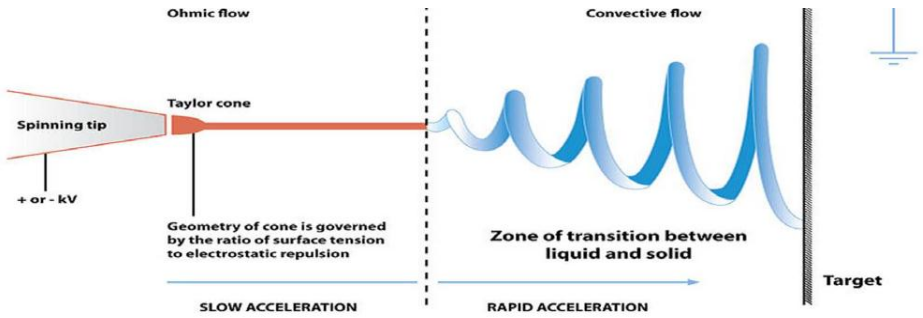


Figure 2: The most used needle electrospinning with the formation of Taylor cone. [10, 9]

Electrospinning is now an attractive way or process to produce polymer biomaterials because of the ability of able to control the morphology, porosity and composition and with electrospinning can prepare long fibers of nano- to micro-meter diameter. The one mentioned above is needle electrospinning because of using the needle and it performs two duties as an electrode for electric field and as an anchor to suspend the solution droplet. There is also a multineedle electrospinning used to increase the production rate of multicomponent nanofibers webs. The productivity of nanofibers production in electrospinning was improved by a straightforward method of increasing the number of needle nozzles but this needs a large operation space and spacing between needles to be careful designed so that strong charge repulsion between jets and adjacent needles can be minimized and can avoid uneven fiber deposition [11]. There is also clogging that frequently happens during the spinning process of multiple of needles causing in-continuous production and large effort of cleaning up. Then needleless electrospinning came around to overcome these problems, working without needles [11, 12]. Practically with the needle based method shown in figure 3, electric field is concentrated on the tip of the needle whereas for needleless electrospinning the electric field is normally concentrated in a large area, thus more jets could be produced at the same time [11].

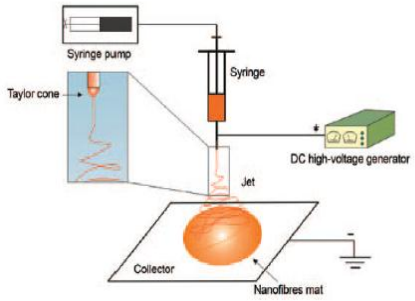


Figure 3: Needle based electrospinning forming single Taylor cone [10, 13, 14]

2.1. Polymer Solution

They significantly influence the electrospinning process and resultant fiber morphology. Viscosity of the solution depends on the molecular weight of the polymer. The higher the molecular weight of the polymer in the solvent, the higher the viscosity. For electrospinning to take place the viscosity should be sufficient so as the molecular weight. When the polymer jet leaves the needle during electrospinning, the polymer is stretched as it travels toward the grounded collector and also entangled preventing the breaking up of electrical driven jet.

The amount of entanglement of the polymer chain is determined by the length of the polymer which has an effect on the viscosity of the solution. An increase in polymer concentration will increase the viscosity of the solution and have greater polymer entanglement. High viscosity will make it hard for the solution to travel increasing the fiber diameter and the solution may dry faster but at low viscosity, can have the formation of beads on the collector. Critical and minimum viscosity and polymer entanglement are necessary for good electrospinning. Surface Tension has the effect of decreasing the surface area per unit mass of a solution and can cause the formation of beads along the polymer jets. If the solvent of high concentration is used then there is greater tendency for the solvent molecules to congregate and form agglomerates due to surface tension. Solvent such as ethanol with low surface tension are preferable for the formation of the smooth fibers. Adding a surfactant to the solution can reduce the surface tension. If the solution conductivity is increased, more charges can be carried by the electrospinning polymer jet. The solution conductivity may be increased by addition of ions such that when a small amount of salt is added to the solution, the increased charges carried by the solution will increase the stretching of the polymer solution and yield fibers of small diameter. Increasing charges will also result in greater bending stability.

2.2. Formation of Jet

Voltage is a critical element in electrospinning. High voltage will induce charges on the solution together with external electric field. It is applied to cause the solution drops to distort into Taylor cone shape during jet initiation. A higher voltage maybe required for stability of Taylor cone but depending on the solution feed rate.

Increasing the feed rate increases the fiber diameter but a lower feed rate is desirable as the solvent will have enough time to evaporate. The higher the voltage applied, the greater the amount of charges that accelerate the jet. Both voltages applied and resultant electric field have an influence on the fiber morphology. Voltage does not only affect the physical appearance of fibers but also the crystallinity of fibers. This happens when electrostatic field start causing polymer molecules to be ordered during electrospinning.

The collector is made mostly by conductive materials that can be electrical grounded. If the collector is non-conductive, charges on the electrospinning jet will quickly accumulate on the collector resulting in fewer fibers deposited on the collector with a lower packing density that those collected on a grounded collector. Porous collector also gives lower packing density unlike smooth surface. Fibers tend to try faster on a porous collector however on a smooth surface the residual solvent will encourage the residual charges to be conducted away to the collector.

Distance between the collector and the tip may or may not have the effect on the electrospinning process and fiber morphology. It has direct influence on flight time and electric field strength. The longer distance means longer flight time for the solution to stretch before depositing on the collector and may also increase the fiber diameter.

Humidity has influence in the polymer solution during electrospinning such that at high humidity water is likely to condense on the surface of the fiber when the process of electrospinning is carried out at normal atmospheric pressure. An increase in humidity can cause circular pores to form on the fiber surface. The pore size increases with humidity until the formation of large non uniform shaped structures. At low humidity, a solvent may dries very rapidly then the evaporation may be faster than the removal of the solvent from the tip of the needle or rod.

Temperature plays an important role to the polymer solution by increasing the evaporation rate and reducing the viscosity of the solution. When PUR is electrospun at high temperature, fibers with uniform diameter are produced. This is because of lower viscosity and greater solubility of the polymer in the solvent resulting in great stretching of the solution.

Pressure surrounding electrospinning jet does not improve the electrospinning but when below atmospheric pressure the polymer solution has a greater tendency to flow out and causes unstable jet initiation [21] and a very low pressure electrospinning is not possible due to direct discharge of the electrical charges.

2.3. Properties of Electrospun fibers

Electrospun fibers tend to possess properties that are different from convectional polymeric fibers because of the influential of varying process parameters. Fibers are collected on a spun bond material by forming a uniform web consisting of randomly oriented, random coiling or looping electrospun fibers. Reneker et al. suggested that the coiled morphology of nanofibers is caused by the looping of the jet. A wide variety of parameters including solution, process and environmental affects the electrospinning process and properties of the forming fibers. Studies have been conducted by several research groups showing the effect of parameters on fiber morphology and fiber diameter. The fiber diameter of electrospun fibers tend to range from tens to hundreds of nanometers but rarely the diameter of less than tenth can be obtained depending on the size of the polymer molecule [6]. Small diameters are preferable when pursuing the largest specific area and Huang et al. noticed that fiber web consisting of the finer fibers also exhibited higher tensile modulus and ultimate tensile strength. The presence of hydrogen bonding also increases the fiber diameter with increasing the polymer concentration has been found to be stronger than expected for non-associative polymers.

Small fibers are obtained with low viscosities that also promote the formation of beads. Beads are most considered as defects need to be eliminated because they cause deterioration of mechanical performance of fibers [22]. The amount of beads can be induced by using additives such as salts, ionic surfactants or additives which may change the properties of the solution.

Additives may reduce the amount of beads but simultaneously reduce the fiber diameter. The higher the polymer concentration results in larger the diameter of fibers. Electrospinning from free surface or from droplet of uncontrollable size also leads to larger diameters of fibers [6].

2.4. Electrospinning Designs

Needleless electrospinning are classified according spinnerets that are called fiber generators: rotating and stationary spinnerets. Figure… below shows different types of rotating spinnerets and focused on cylinder spinneret because jets tend to initiate natural in the optimal position and stationary spinnerets.

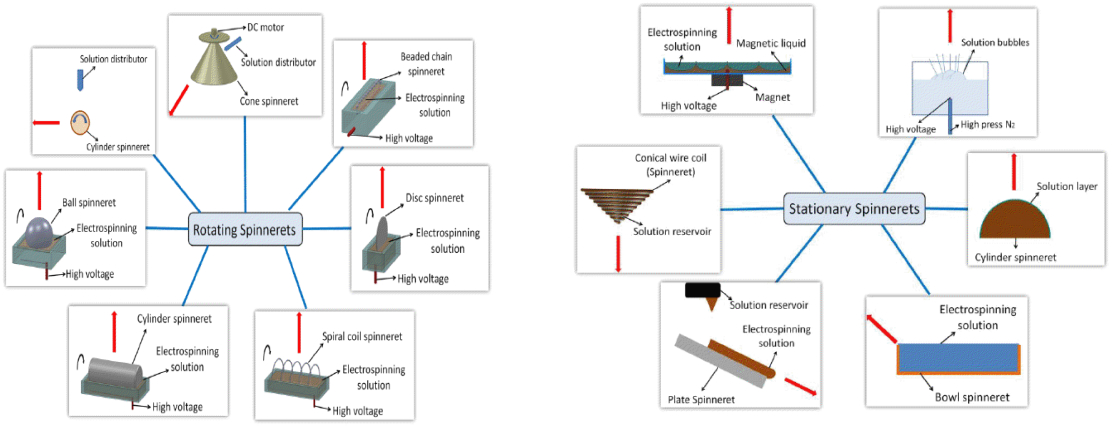


Figure 4: schematic diagram of needless rotating spinnerets & stationary spinnerets [8].

2.4.1. Melt electrospinning

Polymer melt is being used instead of polymer solution remembering that polymer with higher molecular weight forms largest diameter fiber.

A constant heat is applied to the reservoir containing the polymer solution for spinning so that the solution remains in the molten state.

Distance between the collector and the needle is close to 2 cm different compared to conventional (capillary) electrospinning close to 10 cm. Polymer melt tends to be more viscous that polymer solution because of the temperature that able to maintain the polymer in its molten state, thus a greater charge is required for electrospinning jet initiation. Increasing the field strength the resultant fiber diameter is reduced.

2.4.2. Upward needleless electrospinning

The upward needleless electrospinning consists of 2 layer system where the lower layer is ferromagnetic and the upper layer is polymer solution that was subjected to normal magnetic field provided by permanent coil or magnet [15]. Through this procedure a steady vertical spikes of magnetic suspensions perturbed in the interlayer of the interface and the normal electric field being applied then perturbations of the free surface of the uppermost polymer layer becomes the sites of jetting directed upward [16].

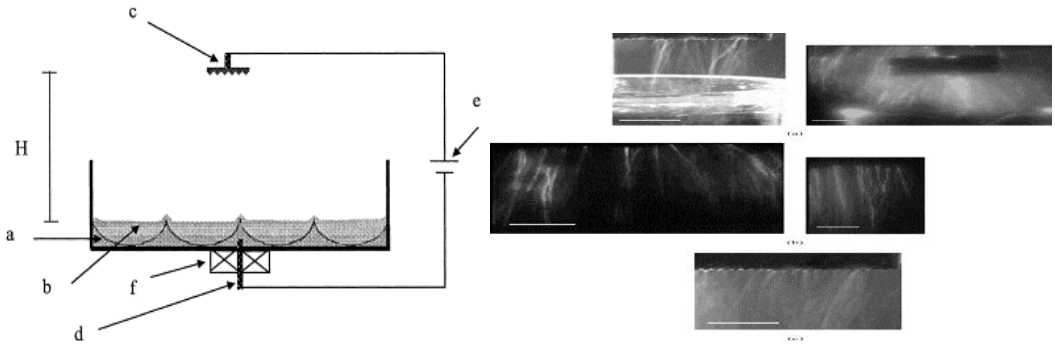


Figure 5: The schematic upward needleless electrospinning (a) Layer of magnetic liquid, (b) layer of polymer solution, (c) counter-electrode located at a distance H from the free surface of the polymer, (d) electrode submerged into magnetic fluid, (e) high voltage source, and (f) strong permanent magnet or electromagnet [16].

2.4.3. Nanospider

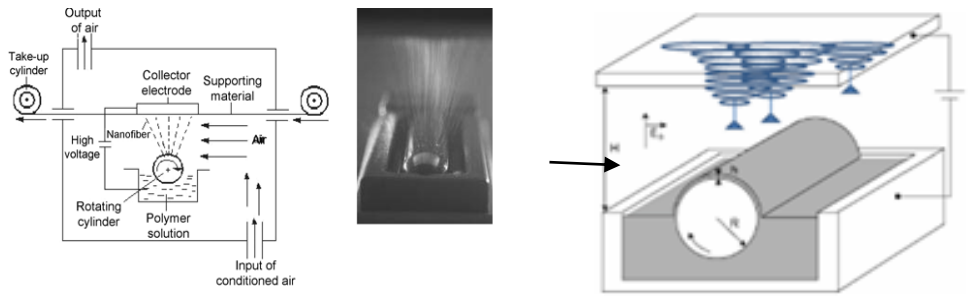


Figure 6: Schematic diagram of Nanospider™ technique designed by Prof. Jir'sak at TUL.

It is a unique and modified electrospinning method that produces continuous nanofibers by using high voltage electrostatic field to create an electrically charged stream of polymer solution or melt. The method was invented based on the possibility of producing nanofibers from a thin layer of liquid polymer. Like all other electrospinning techniques nanospider also has Taylor cones formed at the surface of rotating roller immersed in a polymer solution. Many Taylor cones are formed, unlike with needle electrospinning only one, near to each other throughout the entire length of the roller. The rotation of the roller increases the production ability and is now used in industries. It is a simple and versatile method for production of ultrathin nanofibers from all kind of polymer materials. These polymer materials vary in diameters from 50-300nm when processed to nonwoven web.

2.4.4. Rod electrospinning

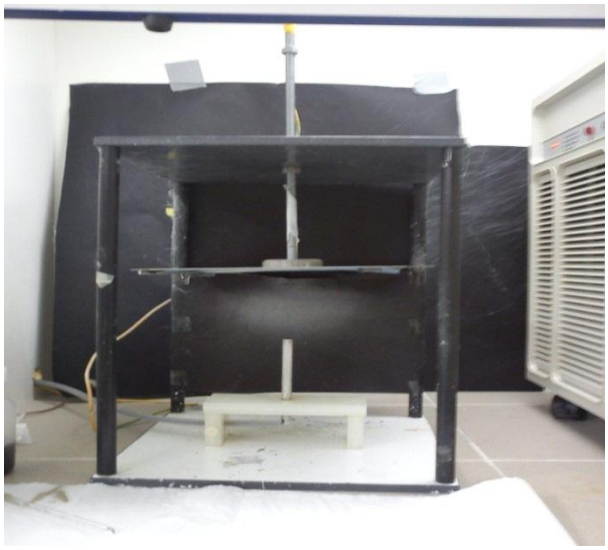


Figure 7: Rod electrospinning of solution into nanofibers under fume cupboard for stability of humidity.

Rod electrospinning is a method used to electrospun fibers as a pre-test before using big methods like nanospider. It is set under the vacuum chamber with temperature and relative humidity reader; voltage applied to it and electronically grounded which affect the electric field that acts to accelerate the charged fluid drop place on tip of the rod depending on the diameter the size of the drop, resulting in a thin jet. It is also done under chamber so that the solution could not dry before being

electrospun. The metal collector is grounded to avoid fibers to move in all direction but to move straight up to the nonwoven square piece place magnetically to the collector plate.

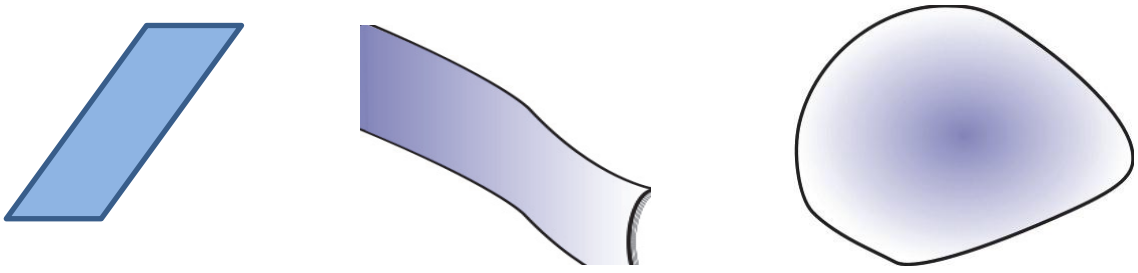
There is an adjustable distance between the rod and the collector. The desirable distance is 10 cm because less than 10 cm, fibers would not get dry before reaching the collector so forming nodes and longer distance will cause the fibers to move in all directions. There are also factors that have effect on the electrospun material. Time is one of them such that more time will result in less porosity and more crosslinking of fibers resulting in better properties unlike with less time. Viscosity of the solution will also affect the material such that if viscosity of solution droplet is high becomes difficult for fibers to jet.

3. Nano- Fiber Composites

In electrospinning processes there are variety of polymers that are used as solutions and soluble in most common solvents under normal conditions. These polymers include PS, PVC, PUR and water soluble such as PVA. It is different with melt electrospinning, polymers applied are those with melting temperature is sufficiently low such as polyesters.

3.1. Composites fibers using nanofillers

There are different types of nanofillers including one dimensional in the form of plate or lamina, nanotube/nanofiber with a diameter less than 100 nm and isodimensional nanoparticles with all dimensions less than 100 nm. The nanocomposites are distributed according to nanofillers as shown below as classified by ISO/ TS27 687 (2008).[17]



One dimensional nanoplate Two dimensional nanofiber Three dimensional nanoparticle

Figure 8: Types of nanofillers used in most nanocomposites [17].

Nanofillers are introduced or dispersed in the polymer matrix or phase at a rate from 1 % to 10 % (in mass) [17].

3.1.1. Composites with fullerenes

Fullerenes are molecules that are covalently attached to polymers in many different ways and require covalent linkages as shown below (figure 9).

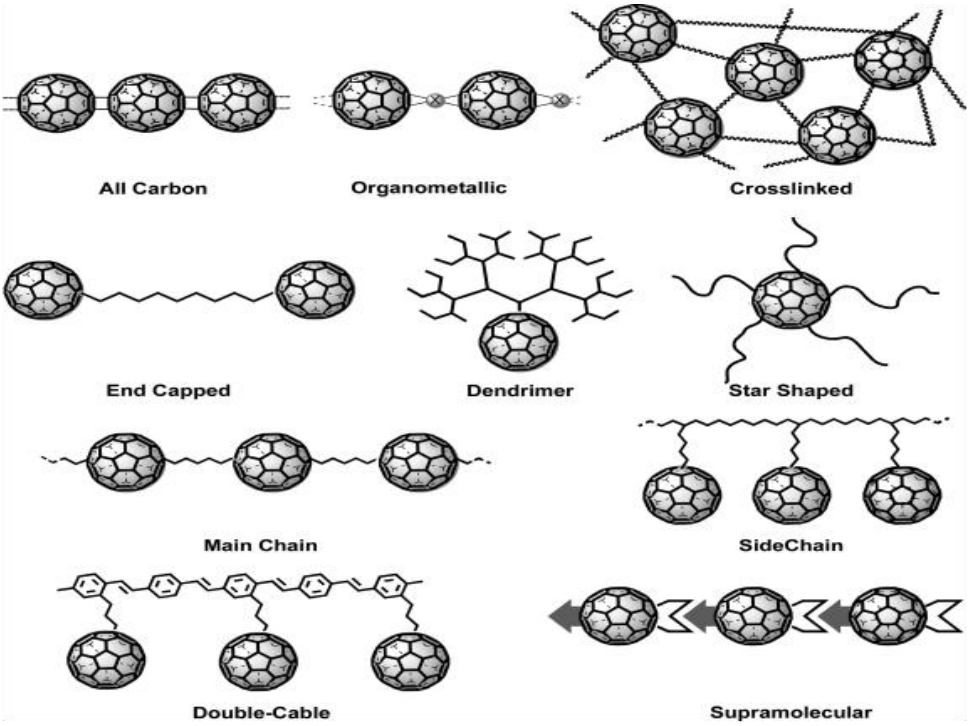


Figure 9: Schematic representation of the different types of C60 containing polymers [6, 18]

Fullerenes are the collection of hollow carbon molecules made of a cage of interlocking 12 pentagons and 20 hexagons with a diameter of 0.71nm and crystal size differ with fabrication methods from 50 to 120nm. C-60, buckyballs are extremely strong molecules, able to resist pressure. They are able to retain their shape after being subjected to over 3,000 atm [18]. They don't bond chemically but they stick together through weak Van der Waals forces like nanotubes and making them compressible. If fullerenes are compressed to certain percentage of the original size, they become more than twice as hard as diamond. Fullerenes can be cross-linked with polymer resins to obtain cross-linked polymers and high performance polymer films. These materials become very hard and thermal extremely stable. This gives them potential as lubricant. When incorporated in

relatively low amount in a polymer matrix they can be held in place and impact some of their strength and low density to the material.

If the fullerene C-60 is in polymer composites a fast photo induced electron transfer occurs from the polymer to C-60 molecules and therefore photoconductivity is observed [6].

C-60 are the easiest to produce and cheapest with prices rising rapidly for larger fullerenes. Fullerenes are insoluble in polar solvents but soluble in alkanes and have excellent solubility in aromatic solvents, carbon disulfide and mostly in benzene.

Fullerene, C-60 can be incorporated into other electrospun nanofibers to produce nanocomposites materials where the matrix is presented by polymer nanofibers and the reinforcement is presented by C-60 [19]. This is done by needle or needless electrospinning technology

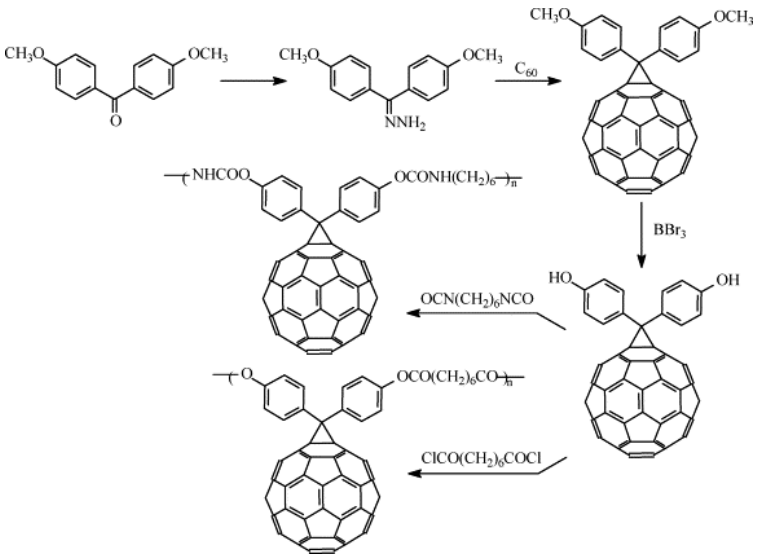


Figure 10: Chemical Reaction of polyester & polyurethane with C60 [6]

Due to their spherical shape, these buckyballs contain high degree of symmetry and can react with numerous compounds. The extra stability of C60 is due to truncated icosahedron structure [18]. C60 can remain unreactive in inert conditions although they show reactivity in numerous organic reactions. The characteristic reaction of C60 as shown in (figure 10) is electrophilic addition at the carbon in the 6,6 double bonds whereby causing a decrease in bond angles. This allows bonds to be more flexible when closing the cage and becomes stable. The unreactive buckyballs are sparingly soluble in many solvent [18] at room temperature such as DMF due to its high degree of interaction with the sphere which leads to greater solubility. The melting point of buckyballs is > 280°C.

Fullerenes exhibit a high degree of mechanical strength and possess high temperature stability as they begin to break down into amorphous carbon particles around 1260°C [18].

Fullerenes endohedral have been included into polymer matrix such as PMMA as shown in (figure 11) to offer unique properties using needle electrospinning. Fullerenes are encapsulated on polymer matrix forming a helix structure.

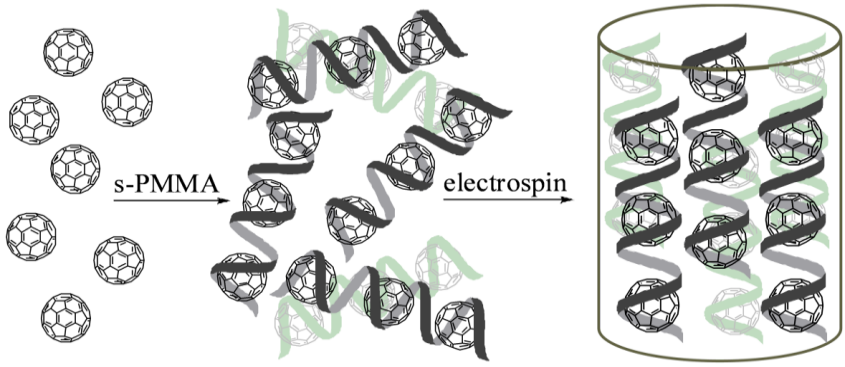


Figure 11: Encapsulation of C60 with helical PMMA polymer [18].

3.1.2. Composites with Nanotubes

Carbon exists in nature as an abundant element. Carbons are produced from polyacrylonitrile (PAN). Carbon fibers have excellent properties, i.e. anisotropic properties, high heat resistance, low coefficient of thermal expansion, high tensile strength and modulus but expensive. Carbon fibers have the option of carbon nanotubes fibers. Diamond and graphite were most considered carbons centuries ago before Kroto in November 1985 discovered C60 then years later 1991, Iijima of NEC in Japan discovered carbon nanotubes possessing extraordinary mechanical, electrical and thermal properties. [5] These carbon nanofibers consist of concentric graphitic layers meaning they were multi-walled carbon nanotubes (MWNTs). Then in 1993, Iijima discovered the synthesis of first single-walled carbon nanotubes (SWNTs). SWNTs have seamless structure and promise to be the next reinforcement fillers for high performance composites. [5]

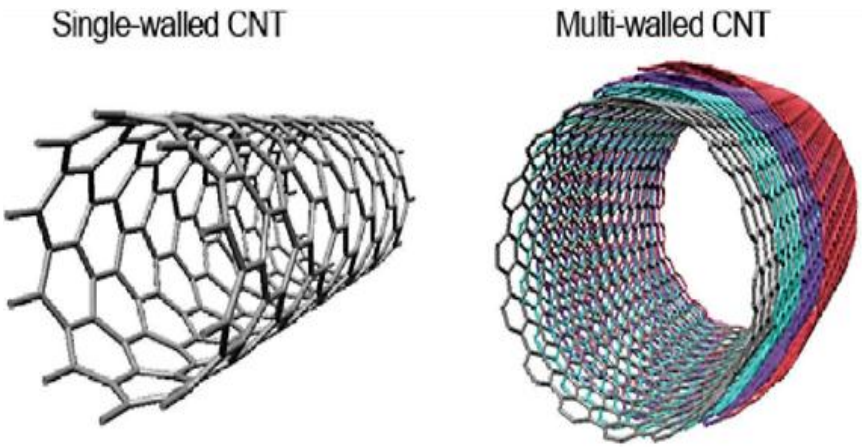


Figure 12: Structures of SWNT and MWNTs [5]

The use of CNTs in a polymer composite is fairly limited because of difficulties in dispersing in the matrix but the percentage is not yet known but recently it's been 15 wt% of carbon nanotubes in the matrix. Carbon nanotubes are characterized by their extremely large surface area that is responsible for their strong formation of agglomerates and strong interfacial interaction with polymer matrix. Therefore to obtain highly efficient nanocomposites need to consider the high level of dispersion, good interfacial interaction and high level of alignment of nanofibers. [5]

3.1.3. Type of polymers used in composite

Polymer matrix composites generally combines high strength, high stiffness fibers (carbon, glass) with low density matrix materials (epoxy, polyvinyl) to produce strong and stiff material that are lightweight. Polymer matrix materials tend to bind fibers and transmit the loads to the fibers through chemical and mechanical bonding. They have low strength and modulus compared to fibers they bind. Polymer matrices are characterized by their advantages as low density, good chemical resistance and corrosion resistance, easy to fabricate, poor mechanical and thermal properties therefore need reinforcement and poor environmental stability.

Polyvinyl alcohol (PVA) is a polymer used as matrix material with low cost and good strength. It is a synthetic semi-crystalline polymer prepared by the polymerization of vinyl acetate, followed by partial or complete catalyzed hydrolysis to remove acetate group. It is hydrophilic; soluble in water therefore has found wide acceptance as an adhesive, hydrogel or membrane. It has a melting temperature of 230ºC but decomposes rapidly above 200ºC [5].

Since we need to consider high level of dispersion in this thesis therefore could be achieved by using PVA. PVA has high strength and high modulus of 250 GPa compared to polymers, i.e. polyethylene (PE).

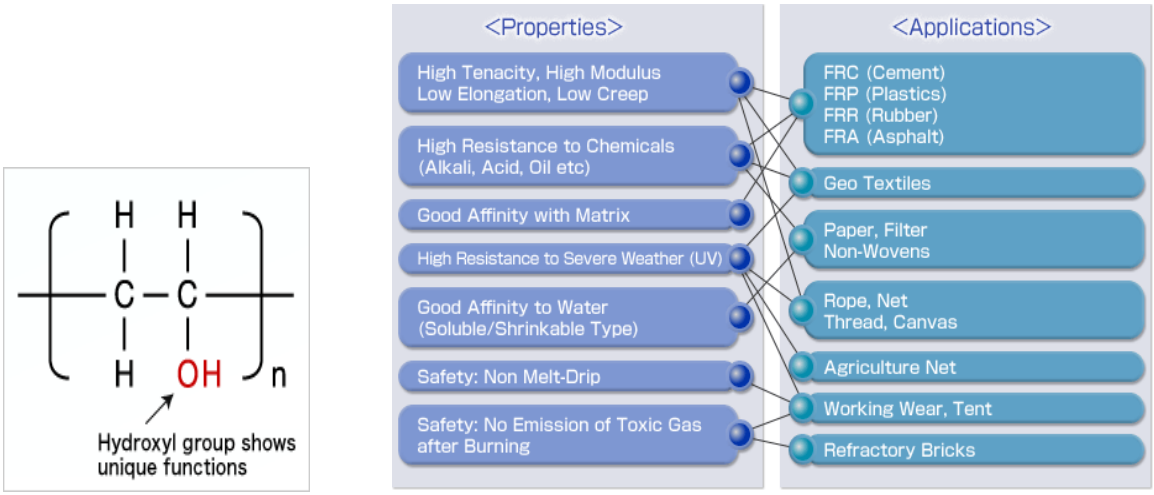


Figure 13: Chemical Structure of PVA and its properties and applications.

[http://www.unitika.co.jp/vinylon/e/vinylon/index.html]

Crosslinking is a vital tool for the modification of existing polymers to achieve new and improved material. PVA is a biodegradable synthetic polymer that acquires special attention because of its good transparency, luster, anti-electrostatic properties, chemical resistance and toughness [20]. Crosslinking of PVA and be easily modified is due to presence of hydroxyl groups that open new domains of application for material.

Polyurethane (PU/PUR) is a polymer that is widely used in biomedical, filtration, protective clothes, composites, sensors, actuators and wound healing applications [1]. In cases where in contact with blood especial wound healing, show of their relative inherent relative nonthrombogenicity of their surface and syntheses very easy to different forms. PUR fibers have shown interest in the healing wound application although previously has problem of fluid accumulation in few days of use. Recently there is been nanofibrous PUR membrane prepared by electrospinning that promote fluid drainage. This is due to high porosity of nanofibrous membrane which allows excellent oxygen permeability [21]

PURs are available in both thermoplastics and thermosets. Thermoplastics PURs are rigid and highly polar because of their linearity with hard and soft segments as a copolymer.

Polyurethane has a melting point of 177-233°C and usual decomposes at about 240°C. During electrospinning there are dominant factors that affect the morphology of the fibers including viscosity, temperature and concentration. The viscosity of polyurethane polymer solution decreases with increasing shear rate.

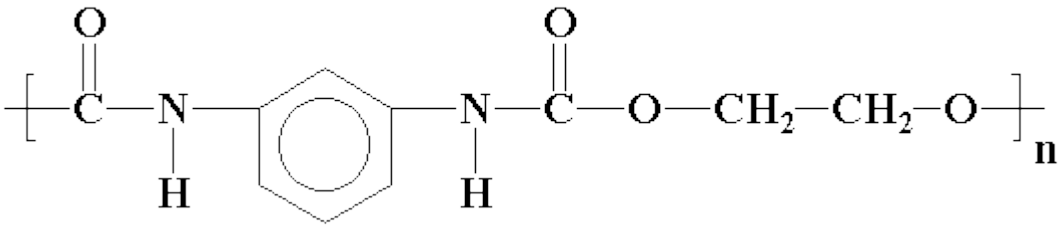


Figure 14: Chemical structure of polyurethane

[http://pslc.ws/macrog/urethane.htm]

3.1.4. Concentration of nanofillers

Concentration of nanofillers in the polymer solutions has some effects causing some changes in electrospinning parameters depending on the mass weight percentage. Nanofillers are introduced at a rate from 1 % to 10 % (in mass) [23]. High concentration may be difficult to spin because of high viscosity causing the formation of agglomerates in the solution known as beads while very low concentration might not cause any effect in the nanocomposites. The amount of fillers is very important when looking at what properties are required of that filler in the polymer solution. High concentration causes high entanglement in the polymer solution yet not so high that the viscosity prevents polymer motion induced by the electric field. The concentration of the polymer in the solution has no greater effect as compared to concentration of fillers because of the certain role they possess in the solution either increase the distance or decrease the electric field which decreases the beads density of fillers.

Applied fields can have influence in the fiber morphology creating variety new shapes on the surface of the material. During electrospinning, applied voltage and solution concentration have effects on the fiber formed morphology.

The voltage strongly correlates with the formation of bead defects in the fibers while the fiber sizes are strongly affected by the solution concentration. Increasing the solution concentration increases the fiber diameter according to power law relationship.

Deitzel et al. investigated as well the formation of beads and found out that the spinning voltage influence mainly the formation of beads while polymer concentration has effect on the fiber size and also noticed that at high concentration a bimodal distribution of fiber sizes was created [3].

The bead like structure is formed when the distance is decreased while the average fiber diameter is increased. When increasing the concentration, the average diameter rises and bead like structure turns into blobs at lower distance. But at high concentration results to failure of fibers instead of being drawn as the viscosity was too high. This may also be the results of high flow rate at lower concentration. Therefore the electrospun fiber morphology is strongly correlated with viscosity, equivalently concentration and temperature as well as addition of salt [3].

Increasing the concentration of nanofillers in the polymer solution increases some properties including thermal conductivity. The type of nanocomposites formed is mostly governed by the nature and concentration of the fillers and also the nature of the polymer and type of surfactant used. In order to improve the distribution of carbon nanoparticles in the polymer matrix is by the use of the right solvent which will subsequent evaporate and also the dispersion of the nanofillers with a powder polymer using ultrasonic in an easily evaporated liquids to prevent the formation of aggregates [24].

3.1.5. Application of nanofillers

Figure 15: Application of polymer nanofibers in different fields

3.2. Thermal Properties on Nanofillers

3.2.1. Thermal conductivity and flammability

There are categories of fillers that are commonly used to fabricate polymer nanocomposites including layered inorganic compounds, nanofibers and nanoparticles [25]. These fillers have exhibit remarkable improvement in the performance. Nanotubes have high thermal conductivity and superior mechanical properties. The thermal conductivity of nanotubes can be influenced by many factors including interfacial bonding, nanotube dispersion, alignment and aspect ratio [26].

Single walled nanotubes (SWNTs) tend to increase their thermal conductivity at room temperature in the epoxy nanocomposites [25]. Researches have little-studied factors that have impact on the effective thermal conductivity of nanotubes which causes thermal resistance between nanotubes.

This originated where thermal energy contained in the high frequency is transfer through phonon-phonon couplings, to low frequency before being exchanged with surrounding mediums. The thermal resistance posed by nanotube polymer interface was equivalent to resistance of a polymer with thickness of 20 nm which indicated that the heat transported in the nanotube based nanocomposites material will be limited by the interfacial thermal conductance. Nanotubes as filler particles can also increase thermal stability of polymer matrices in the nanocomposites by absorbing a disproportionate amount of thermal energy thereby retarding the thermal degradation of a polymer.

Flammability has become polymer's defect making them easily ignited by external heat or fire. Studies have shown interest on flame retardant polymeric materials by employing a small amount of nano-additives. Nanotubes are proven to be an effective flame retardant addictive's such that even small amount of MWNT greatly improve flammability of PP [11]. MWNT effectively prolongs the burning of PP. The improvement in flammability to nanotubes networks the spanning the nanocomposites that dissipate heat and thereby reduce the external radiant heat transmitted to the PP sample. The flame retardancy of CNT is due to the formation of a network structure of CNT in the polymeric matrix during combustion [11].

Carbon nanotubes are among the additives that provide unique opportunities to improve mechanical, electrical, and thermal properties of a variety of polymer matrices [12]. The properties of nanotubes/polymer nanocomposites strongly depend on the nanotube dispersion/concentration within the matrix. Carbon nanotubes exist as macro-molecules of carbon and chemical bonded giving them unique strength. They are organophilic and can be dispersed into the polymer.

Carbon nano-additives including CNT and fullerenes (C-60) have become highly attractive in industries and academic because they increase the flame retardancy of nanocomposites [25]. CNT has been employed to prepare for high performance fire resistant materials because of its one dimensional geometry nano-material and fiber network that formed in the condensed phase.

Fullerene (C-60) has been prepared as zero dimensional carbon particles for nanocomposites to improve flame retardancy. Fullerene can concurrently enhance the thermal properties, delay the thermal oxidation degradation, improve flame retardancy of polymer and slow the combustion process of polymeric materials. Fullerene C-60 has free radicals that are trapped during the mechanism. The C-60 acts as a radical sponge to trap the macromolecular or other radicals created from pyrolysis of polymer or when quenched many kinds of free radicals that are produced from the degradation of polymer chain therefore delaying the speed of combustion. C-60 can significantly extend the ignition time and reduce heat released.

The small amount of C-60 can greatly improve the thermal stability and flame retardancy better than carbon nanotubes. This is due to the trapping of free radicals and the cross-linking network during combustion of C-60 [7].

Besides barrier effect, free radical trapping and network structure of nanoparticles, the correlations between flame retardancy and fine structure of polymers, varying viscosity during thermal degradation and combustion need further research [27].

3.2.2. Thermal degradation & Flame retardancy of Polyurethane/C-60

Polyurethanes (PURs) are either thermoset polymers produced by the reaction of isocynates with polyols or thermoplastic mostly versatile elastomeric materials. PUR thermal decompose or degrade as temperature increases and there is weight loss of the polymer material at different temperatures and atmospheres.

Therefore the incorporation of C-60 effectively reduces the heat release rate of the polymer and results in longer time to ignition of the material. Why? It is because the C-60 can trap many free radicals that are produced during the decomposition of polymer material when experiencing free radical chain reaction.

If these free radicals created are trapped immediately during the degradation of polymer would practically improve the thermal stability and thermal oxidation of polymer. Hence C-60 incorporation could delay the decomposition process of polymer both in nitrogen and in air and it prolongs the time to ignition making it an advantage over CNTs and clay for improving the flammability of polymer [27].

CNTs and clay form network structure in polymer matrix when exposed to high heat or flames thereby reducing the flammability of polymer because the network covers the polymer substrate preventing heat or oxygen entering the polymer but with C-60 is different [4, 25].

Since C-60 is in a spherical shape molecule so cannot form the network structure in a polymer matric but will only trap free radicals in order to enhance the thermal properties and improve flame retardancy of polymer nanocomposites. It does this during the process of polymer degradation at given temperatures.

Thermal stability of a material is defined by the specific temperature or temperature-time limit within which the material can be used without excessive loss of properties. The degree of thermal stability of polyurethane depends on size, shape, nature, amount of filler used, dispersion uniformity, as well as the degree of interaction between the inorganic filler and the matrix. Therefore the nano-scale fillers are used for ideal performance for uniform dispersion throughout the matrix and interact strongly with the organic matrix [26].

According to the fullerene C-60 structure can produce thermally stable PUR nanocomposites because of it radical scavenging efficiency [25]. The incorporation of fullerene C-60 into PUR matrix is important because it allows the combination of a single material with unique properties with that of well-known polyurethane. PUR is one of the additives/fillers known as flame retardant that able to delay the flashover from the surface combustible. Flame retardant keeps the flame from spreading at minimum rate and prevents sustained burning thereby increase the resistance of ignition of a polymer material. The flame retardant of a polymer material will then depend on the structure of the component, the amount of filler and the density of a material [25, 26].

3.2.3. Factors affecting flame retardancy of polymer nanocomposites

There are many factors that affect the flame retardancy of polymer nanocomposites including the dispersion of nanoparticles in the matrix such that can significantly reduce the heat release rate, the use of organic intercalating agent (ammonium salt) into the clay of dispersion of polymer matrix reducing the ignition time when burning and finally the polarity and viscosity of polymer itself [4].

High polarity of polymers is favorable to the dispersion of organic clay in matrix and the high melt viscosity of polymer favors flame retardancy on certain conditions such that the flame retardancy is achieved by dripping of a material. High melt viscosity also increases the level of dispersion of nanoparticles making it difficult.

3.2.4. Different tests used for thermal stability

Cone calorimetry test is widely used to evaluate the performance of fire retardant polymers. The principle behind is based on measurement of decreasing oxygen concentration in the combustion gases of a material subjected to high heat flux. There are different parameters that are evaluated including ignition time, heat release rate, specific extinction area, the ignitability, combustibility, the smoke production and the production of toxic gas [4].

Limiting Oxygen Index (LOI) is also used for evaluation of the flammability of material. The higher the LOI index the better the flame retardancy whereas the lower the LOI the more flammable is the material.

Oxygen Index = [O2] / ([O2] + [N2]) * 100…….. (1)

Thermo gravimetric analysis is used to evaluate the amount and rate of change in the weight loss or gain of material during decomposition process or oxidation process as a function of temperature or time in a controlled atmosphere (oxygen or air). This is done in order to determine the composition of a material and able to predict their thermal stability at temperatures up to 100°C [4].

4. Material Applications

4.1. Nanocomposites

Figure 16: Different application fields of needleless (Nanospider™) electrospinning materials [28].

Nanofibers were mostly developed for above applications as shown in (figure 15) above but because of their unique properties they are even spreading and have many opportunities. The focus of this thesis is based on protection clothing for flame retardancy and as for antibacterial materials.

5. EXPERIMENTAL PART

The experimental part was devoted to production and testing of composite nanofiber materials with thermal resistivity caused by the presence of spherical fullerenes with and without different surface modifications in different polymer matrices using different electrospinning production processes. The produced composite nanofibers were compared with the blind samples of different polymer solutions.

5.1 Materials

The two different polymers (polyurethane & poly (vinyl alcohol)) were used as a representative of water as water insoluble and water soluble polymers. The polyurethane (PUR) was used with DMF solvent and $C60Br_{24}$ as a filler and poly (vinyl alcohol) was used with distilled water and C60-OH as filler. The surface properties were changed by surface modifications. The important role of surface modification was to prepare good dispersion of nanofibers in the solution and produce nanofibrous material by means of needleless electrospinning. Hydrophobic PUR chemically reacted with hydrophobic DMF solvent for better stability and Hydrophilic PVA chemically reacted with distilled water to create polar bonds. Fullerenes (buckyballs) are sparingly soluble in many solvents such as DMF at room temperature due to high degree of interaction with the sphere which leads to great stability.

For this research, the polyurethane (PUR, Larithane LS 1086, aliphatic elastomer based on 2000 g/mol, linear polycarbonated diol, isophorone diisocyanate and extended isophorone diamine solution of 30 wt %), was used as a polymer, dimethylformamide (DMF) as a solvent and tetraethylammoniumbromide (TEAB) was used as salt for increasing electrical conductivity of final polymer solution. All PUR solutions were prepared at 15wt% concentration with dimethyformamide (DMF) solvent.

The second polymer used was polyvinyl alcohol (PVA, Mowiol 18-88, DE 13 010 631, 500g net with molecular weight of 13000 g/ml). The surfactant (Slovasol 258/9) was used for decreasing final dispersion in the solution by easing surface tension. The preliminary experiments showed that it was impossible to electrospun these solution without the addition of surfactants during needleless electrospinning under normal conditions.

Cross-linking agents used were glyoxal (3 wt % of PVA amount in the solution of pure 40 wt% of glyoxal in water, Mw = 58.04, d=1.265, bp= 104) and phosphoric acid (4 wt % of PVA amount in the solution of 85 wt % of phosphoric acid in water, Mw=58.00).

Spherical fullerenes C60 with and without surface modification where used. The SIGMA-ALDRICH (483036-1G) fullerene C-60 ~98% purity and $C60Br_{24}$ from SES Research Houston USA of purity 99,5% were used as reinforced nanoparticles in non-water polymer solutions.

Two different solutions of C60-OH in water were prepared at State Office for Nuclear Safety in Prague. The original spherical fullerene was obtained from SES Research Houston USA of purity 99,5%. The first solution in water had concentration of 0.1345g/l and second one with better homogeneity in water had concentration of 320.4 mg/l (but weakly acidic as a rest from C60 oxidation by means of peracetic acid). The original C60 and C60-OH structure are shown in (figure 17).

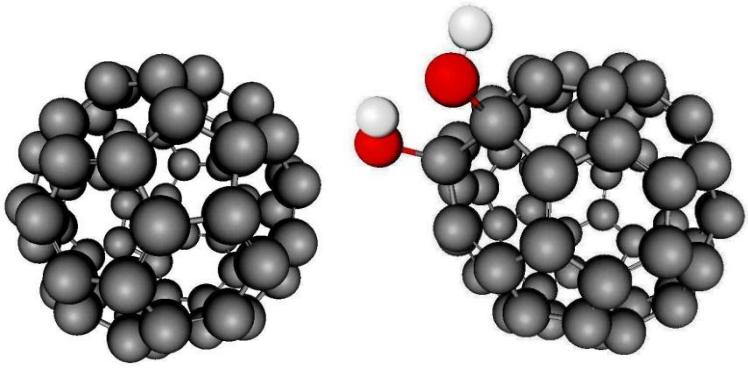


Figure 17: Schematic diagram of 3D structure of spherical fullerene C60 (left side) and spherical fullerene C60 modified by OH groups. Grey dots represent carbon elements, red dots represent oxygen and white dots represent hydrogen.

5.2 Methods

Given in this chapter is the description of solution preparations and electrospinning techniques used for production process under certain conditions.

5.2.1 Production of PUR based nanofibrous layers

PUR solution of 15 wt % used in this research was prepared in the lab by first mixing solvents, 50g of DMF, 55g of DMF + TEAB and 5g of water and then 115g of PUR (30 wt. % PUR in DMF). The blind sample PUR was prepared and rod electrospun (see chapter 2.4.4) with applied voltage of 25.6 kV at 26.6°C temperature and ~ 49% RH in a chamber. The rod electrospinning included a collector that was grounded and diameter of the rod was 0.9 cm and the distance between the rod and the collector was ~10 cm.C-60Br_{24} were prepared and electrospun by using rod electrospinning method.

The second group that was prepared contained PUR with 1, 5 and 10 wt. % of C-60. The 0.15g of C-60 was mixed with 20g and 100g of PUR solution. It took 24hrs for better mixing. The 1 wt. % C-60 was then taken for rod electrospinning with applied voltage of 30.2 kV at 24.6°C temperature and 32% RH. The 5 wt. % was also rod electrospun with voltage of 30.3 kV at 27.4ºC and 20% RH. To achieve thick layer with less porosity required more time in order to have cross-linked material for better properties. The nanofibers layers were collected on a spun-bond material (nonwoven) for better separation.

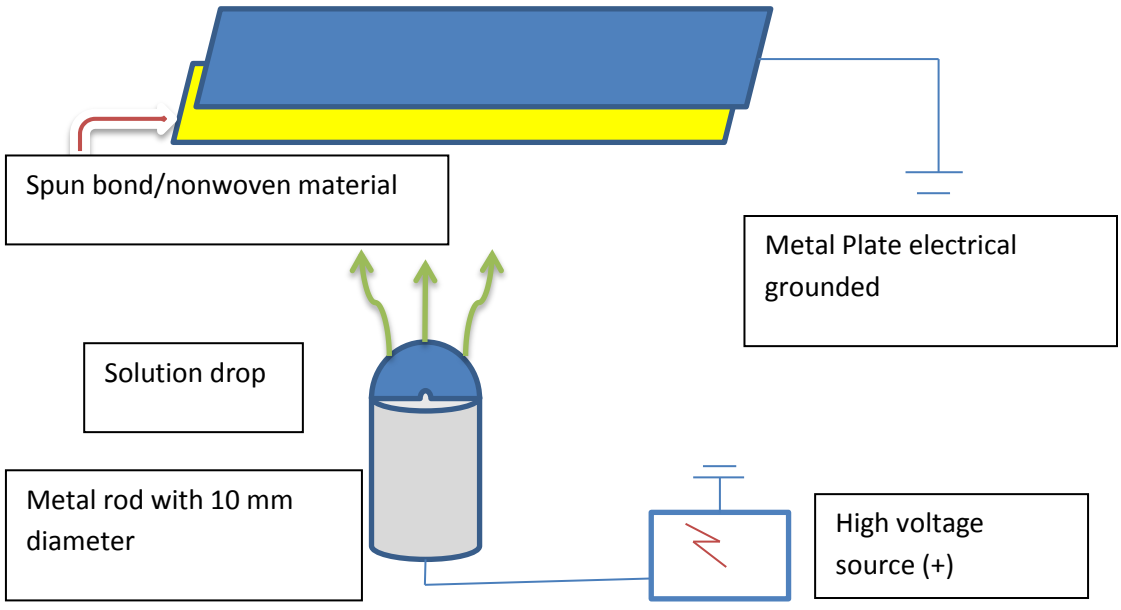


Figure 18: Schematic diagram of rod electrospinning

A second needleless electrospinning technology (see figure 19), cylinder electrospinning (Nanospider) that represent industrial processing was used for 1 and 5 wt. % C-60 PUR solutions. The rotational cylinder that was used had small pick out steel pins all around for the formation of Taylor cones. The distance between the grounded collector and rotational rod was 12cm. The voltage applied during spinning was 52.8kV for 1 wt. % C-60 at 22.3ºC with 19.6 % RH and for 5 wt. % the voltage was 52.0 kV at 18.7ºC with 21.1 % RH. The samples were taken for scanning under electron microscope (SEM) but were first coated with gold preventing ray absorption by samples. The diameters of nanofibers were measured using NIS system (Lucia G Version 4.82) to compete the average and the standard deviation of about 50 measurements.

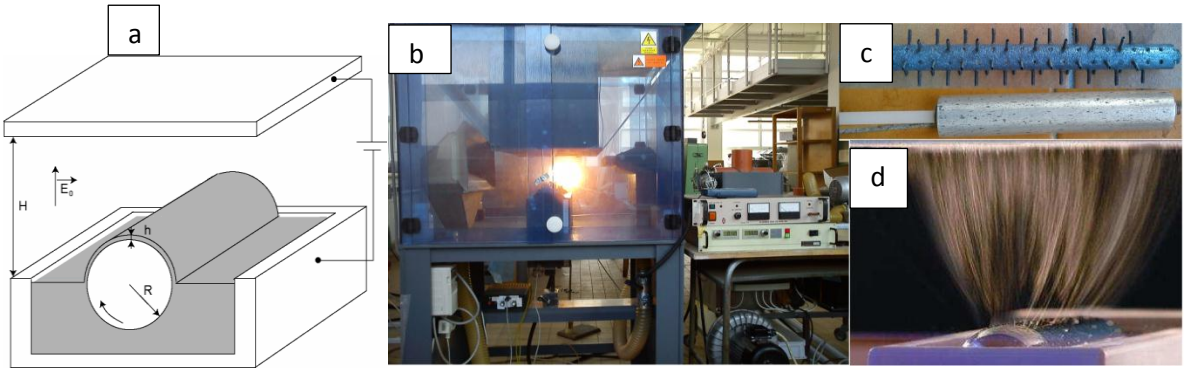


Figure 19: Schematic diagram of nanospider electrospinning (a) a photo of real device (b) a photo of electrospinning process from Nanospider (c) cylinder with spikes and smooth cylinder (d) jetting of fibers taken from www.elmarco.cz .

5.2.2 Production of PVA based nanofibrous layers

The blind sample was prepared by heating 400 ml of water at 70-80°C and adding 4g of PVA to make a 10 wt % solution. The following solutions were prepared using solutions of C60-OH in water. The 4g of PVA was added to 36ml of 0.1345g/l C60-OH solution at temperature range of 70-80°C. For the second one 4g of PVA was added to 36ml of 320.4mg/l C60-OH solution. The sonication process was made for completely separation of agglomerates of nanofibers inside the solution. Solutions were magnetically stirred for 2 days for good homogeneity. The solutions were then electrospun using cylinder electrospinning (nanospider). The PVA was electrospun under normal conditions including relative humidity and temperature.

The distance between the cylinder (smooth cylinder was used) and the collector was 12 cm and voltage applied range from 50.9 kV for blind sample, 52.6kV for 0.1345g/l C60-OH 10wt % PVA and the last one was 54.8kV for 320.4 mg/l C60-OH 10 wt % PVA shown below (figure 20). The surfactant (three drops-0.12g of Sloviol) was added to the solutions for decreasing surface tension during cylinder electrospinning and better jetting of fibers. The PVA is soluble in water and was prepared without adding the crosslinking agents.

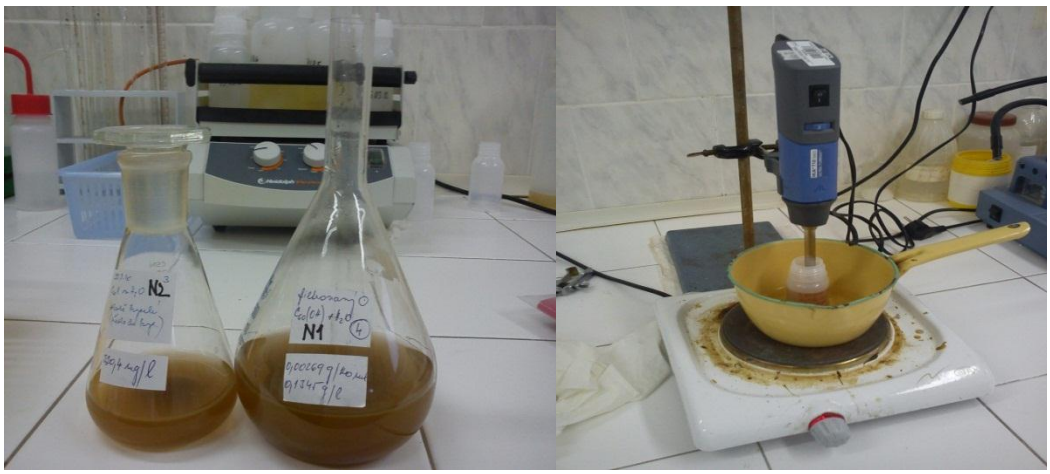


Figure 20: C60OH water solutions and solutions preparation.

The following preparation crosslinking agents (glyoxal and phosphoric acid) were added but being careful of C60-OH degradation. The glyoxal and phosphoric acid were added to 3 different solutions prepared as it was written above. First agents were added in blind sample of 4g of PVA solution. Secondly were added in 0.1345g/l C60OH (4g of PVA) and in 0.3204g/l C60OH (4g PVA) solutions. All the solutions were electrospun using Nanospider method under normal conditions at room temperature 25.5°C and RH was 34.0%. The velocity of support nonwoven movement was 0.05m/min. The voltage applied was 59.6 kV for blind sample and 56.0kV for other 2 solutions. The 3 drops of surfactant were added in each 3 solutions for surface tension. The nonwoven samples resulted from electrospinning were heated in the oven at 135°C for only 4 minutes for crosslinking of the PVA nanofibrous layer (stabilizing against water). This temperature acted as a critical point whereby below material changes and above fibers change colour until reaches a stage where degradation starts.

Table 1: All tested solutions, their parameters and electrospinning conditions

Polymer	*Solvent*	*Concentration of polymer in solution (wt %)*	*Fullerene (wt %)*	*Other additives (surfactant, crosslinking agents)*	*Rod electrospinning applied voltage(kV), temperature (°C)& Humidity (%)*	*Cylinder electrospinning applied voltage(kV), temperature (°C)& Humidity (%)*
PUR (blind sample)	DMF	15	0	Slovasol	25.6, 26.6, 30	
PUR	DMF	15	1 (C60Br)	Slovasol	30.2, 24.6, 32	
PUR	DMF	15	5 (C60Br)	Slovasol	30.3, 27.4, 20	
PUR	DMF	15	10 (C60Br)	Slovasol	No measurements	
PUR	DMF	15	1 (C60)	Slovasol		52.8, 22.3, 19.6
PUR	DMF	15	5 (C60)	Slovasol		52.0, 18.7, 21.1
PUR	DMF	15	10 (C60)	Slovasol		No electrospinning
PVA (blind sample)	Water	10	0	Phosphoric acid, glyoxal & slovasol		59.6, 25.5, 34.0
PVA (crosslinked)	Water	10	0.13 C60-OH	Phosphoric acid, glyoxal & Slovasol		56.0, 25.5, 34.0
PVA (non-crosslinked)	Water	10	0.13 C60-OH	Slovasol		52.6, 25, 30
PVA (crosslinked)	Water	10	0.32 C60-OH	Phosphoric acid, glyoxal & Slovasol		56.0, 25.5, 34.0
PVA (non-crosslinked)	Water	10	0.32 C60-OH	Slovasol		54.8, 25, 30

5.2.3 Analysis for nanofibrous layer characterization

Scanning electron microscope (Phenom G2, Phenom-World BV) was used for structure analysis of the samples. The samples were prepared by placing them in small pin mount stands as shown in (figure 21) and the samples were coated with gold so that samples are electrically conductive and electrically grounded to prevent the accumulation of electrostatic charges at the surface. According to final images, orientation of fibers was visible and mainly fibers diameters were measured

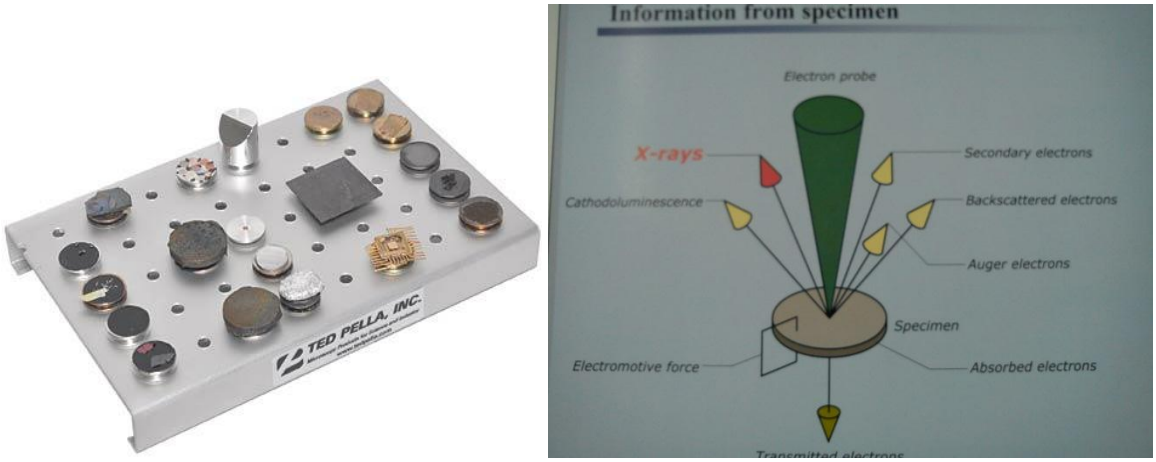


Figure 21: Image of SEM sample preparation [http://www.tedpella.com/SEMmod_html/15012.htm]

And [http://www.jeol.com]

The nanofibrous layers were tested by SEM-EDS analysis and Raman spectroscopy for providing the presence of fullerene inside the produced materials. They were measured at Budapest University of Technology and Economics. SEM-EDS analysis is used for the elemental analysis or chemical characterization of a sample and provides an experimental determination of a specimen's elemental composition [31]. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. The more elements are positively identified in the SEM-EDS experiment, the more narrow the selection of candidate phases will be. To simulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons or a beam of X-rays is focused into sample being studied shown in (figure 21) [29, 30].

Raman spectroscopy is used to study vibrational, rotational and other low-frequency modes in a system and is based on laser interaction with the sample under the classical light microscope. The light impinges upon a molecule and interacts with the electron cloud and the bonds of the molecules. If the final vibrational state of the molecule is more energetic than the initial state then the emitted photon will be shifted to a lower frequency in order for the total energy of the system to remain balanced.

If the final vibrational state is less energetic than the initial state then the emitted photon will be shifted to a higher frequency. The pattern of shifted frequencies is determined by the rotational and vibrational state of the sample [31]. The Raman spectroscopy used was Horiba JOBIN Yvon-LabRam IR with Olympus BX41.

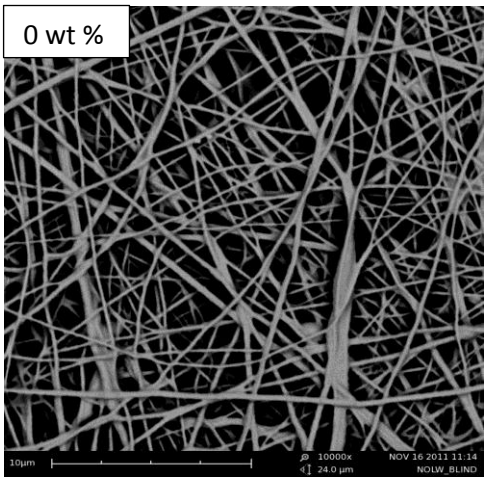
Thermogravimetric analysis is the act of heating a mixture to a high enough temperature so that one of the components decomposes into a gas which dissociates into the air. It is used to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in the materials, decomposition points of explosive and solvent residues [32]. A change of thermal stability of the produced nanofibrous material was assessed at Fire rescue service of Czech Republic by means of TGA. The method is based on measurements of weight loss and relaxed-consumed thermal energy depending on used temperature and time. The tests were performed according to accredited methods, apparatus STA 1500 THASS.

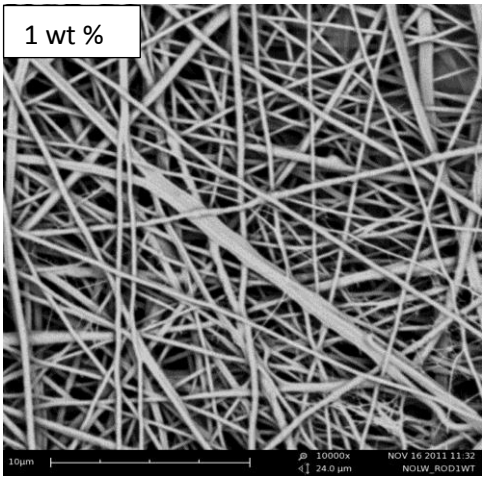
The used degradation medium was air; used temperature regime went from 25°C to 550°C and sample-heating was 10°C/minute.

6. RESULTS & DISCUSSION

6.1 Analysis of fullerene into PUR polymer matrix

Nanofibers were electrospun as discussed in the experimental section using rod electrospinning of different weight percent of fullerenes with the surface modification of bromine, C60Br24. SEM images (see figure 22) identify the random orientation of fibers. The diameter of fibers was measured by means of image analysis and the final results indicated the change in diameters as the concentration of fullerenes increases (see figure 22). Formation of beaded fibers increases as the concentration increases. The PUR solution was first spun in the absence of C60 forming small diameter random fibers. The formation of beads started to show and an increase in fiber diameter as the concentration of C60 into polymer matrix increases from 1 wt % to 5 wt %. There was change in diameter or fiber morphology due to temperature, applied voltage and concentration rate.





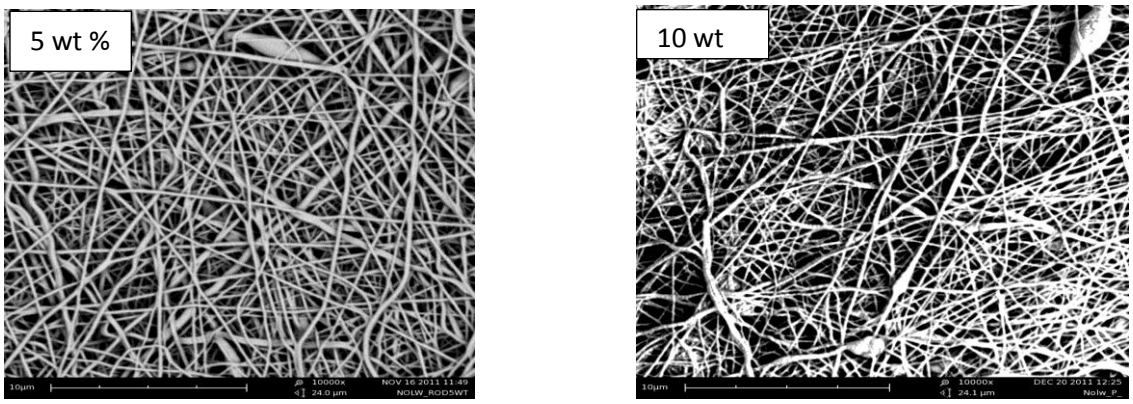


Figure 22: SEM images as examples of PUR solution with the wt % increases (0- 10) of fullereneC60Br24. The rod electrospinning was used for production of these samples. The scale in the SEM images is 10µm.

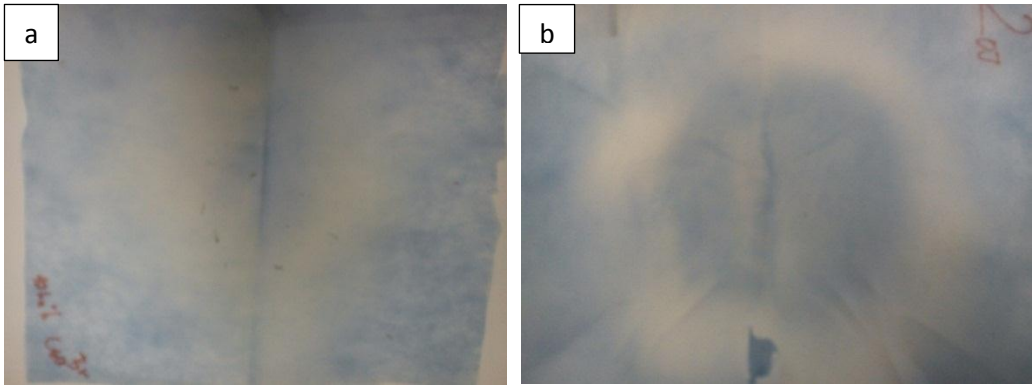


Figure 23: Rod electrospun nanofibers photos, a) 10 wt % of C60 PUR solution showing big droplet of voltage spikes on the surface (b) 1 wt% of C60 PUR solution better spun thicker material.

The 10 wt % of C60 had many defects on the fiber surface and difficult to electrospun. A high concentration leaded to failure of fibers instead of being drawn perfectly. This was due to applied fields that influenced the fiber morphology creating new shapes on the surface and voltage strongly correlated with the formation of bead defects in the fibers. This also contributed to diameter change instead of increasing according to the power law relationship but was decreased.

Table 2: Average fiber diameter measurements [nm] of PUR solutions

	Diameter [nm]	Diameter [nm]
C60 concentration [%]	Rod electrospinning	Nanospider
0 wt %	194.72±65.90	189.90±54.52
1 wt %	223.46±91.38	202.79±79.02
5 wt %	234.28±69.99	227.01±88.02
10 wt%	151.14±43.40	

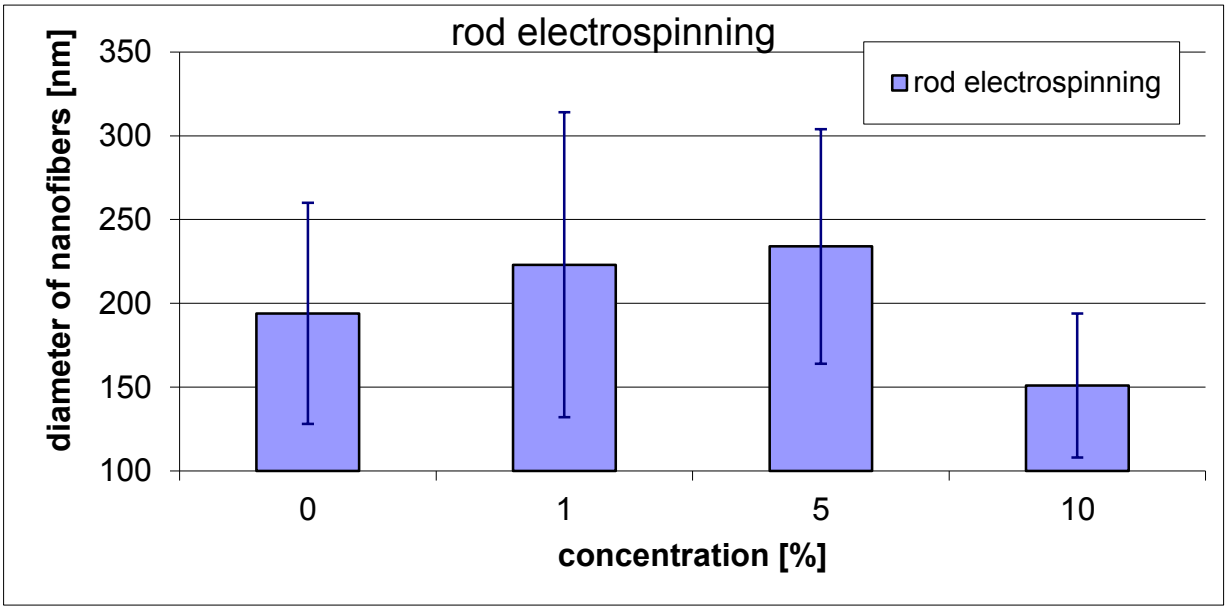


Figure 24: Change of nanofiber diameter with change of concentration of C60Br24 inside the sample.

The production of C60 modified by bromide is more difficult than modification with OH. The final price is higher, thus the C60Br24 was used only to the smaller amount of solution for rod electrospinning. The main reason why to use it as a first filler material into nanofibers was the usage of relatively simple and available analysis for presence of C60Br24 in the nanofibers, SEM-EDS analysis, could be used. The SEM-EDS analysis cannot recognize fullerenes based only from carbon or modified by OH groups because carbon, oxygen and hydrogen are present in the sample of nanofibers. The C60Br24 was used into PUR because of its surface characteristics. The spectrum graphs below show elements that were present in the PUR solutions with C60Br24. The spectrum graphs were used to compare samples showing if fullerenes are inside nanofibers or not.

The comparison from the spectrum analysis in the (appendix 1) showed no significant between blind sample and sample with 1 wt % C60Br. Therefore 1 wt % of C60Br made no or small effect in the PUR solution and even SEM image showed no formation of beads which caused by concentration of C60Br. The spectrum graph of 5 wt % and 10 wt% C60Br (see appendix 1) showed a peak of Br concluded that fullerenes were inside nanofibers compared with PUR without C60Br (blind sample). These fullerenes were not uniformly distributed resulting in the formation of beads as defects.

This means that there was no good distribution of fullerenes in the PUR solution and also means that as the concentration of fillers increases the viscosity increases, resulting in failure when fibers are drawn. The Raman spectra were done too for comparison of PUR blind sample and PUR with fullerenes C60Br24. The Raman Spectrum and images of PUR solution is shown below without fullerenes. This spectrum shows more inhomogeneity which of fullerene agglomerates.

When the rod electrospinning of the solution with C60Br24 showed that the electrospinning is possible for such solutions for production of composite nanofibers, the possibility of usage of industrial electrospinning (nanospider) was used. The nanospider technology requires very good dispersed nanofillers in the solution and need bigger amount of solution. This is why pure C60 was used and it was dispersed inside the solvent (DMF) by help of ultrasound.

SEM images of C60 present in the PUR polymer matrix from nanospider electrospinning production are given in the (figure 25). The cylinder electrospinning was done for 1 wt % and 5 wt % of C60 in the presence of surfactant for easing up surface tension and preventing sparks of electric fields to course defects in the fiber surface. Since 10 wt % was difficult to spin with rod electrospinning as a sub technique of needleless electrospinning it was then excluded in the nanospider electrospinning. C60 are very difficult to process at high concentration due to their lack of solubility and highly aggregating in other matrices [18]. The surface density of the produced sample was about 2 gm^{-2}.

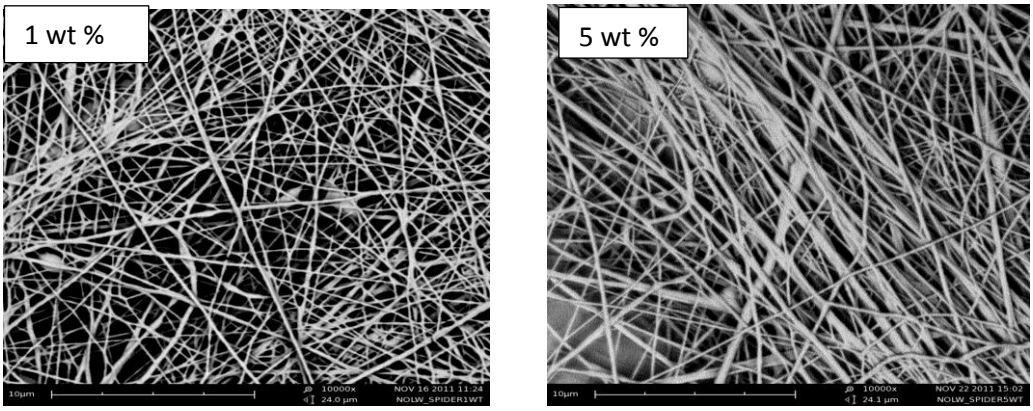


Figure 25: SEM images from Nanospider with increase in diameter

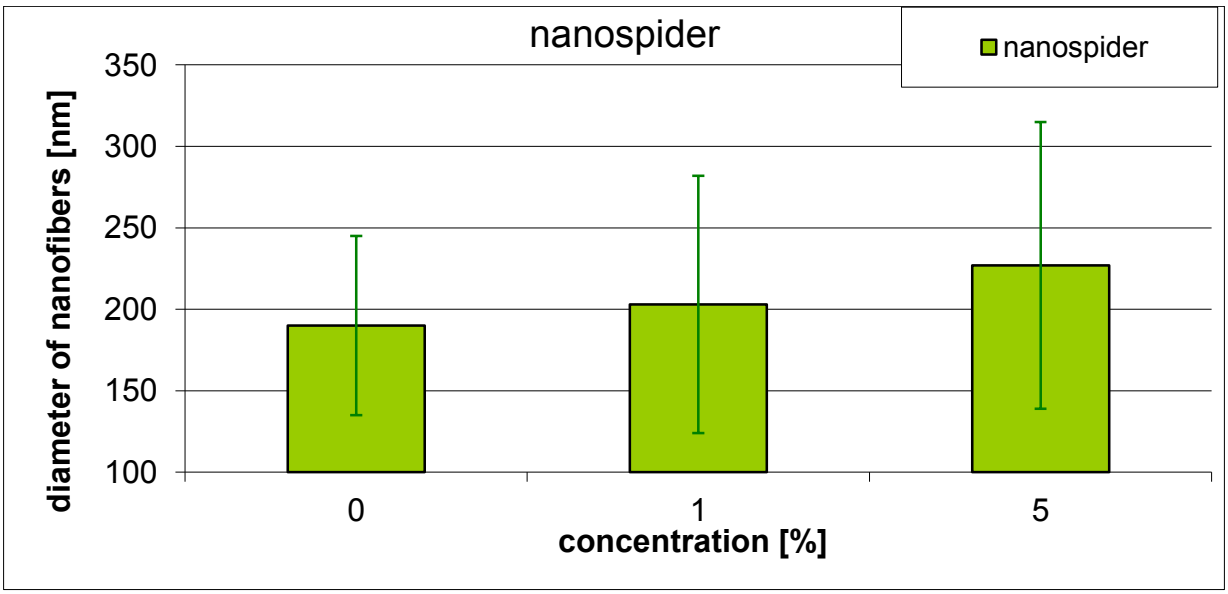


Figure 26: Change in nanofiber diameter with change of concentration of C60 inside the sample.

Although defects were present in the fiber surfaces but diameter sizes increased because of concentration which is found to be relatively larger effect on fiber diameter than any other parameters. As the fiber diameter increased it then created less porosity in the fiber material. The average fiber diameters and standard deviations were calculated using Lucia G Version 4.82 and 50 diameter measurements were taken for each sample to determine the effect of fullerene fillers on nanofiber diameter of polyurethane. It can be seen from the table 2 that average fiber diameter increases with fullerene concentration linearly except for 10 wt % because of resistance to spinning resulting to failure of fibers. It can be seen from SEM images (figure 25) that fine fibers are obtained when concentration is very low of 1 wt %.

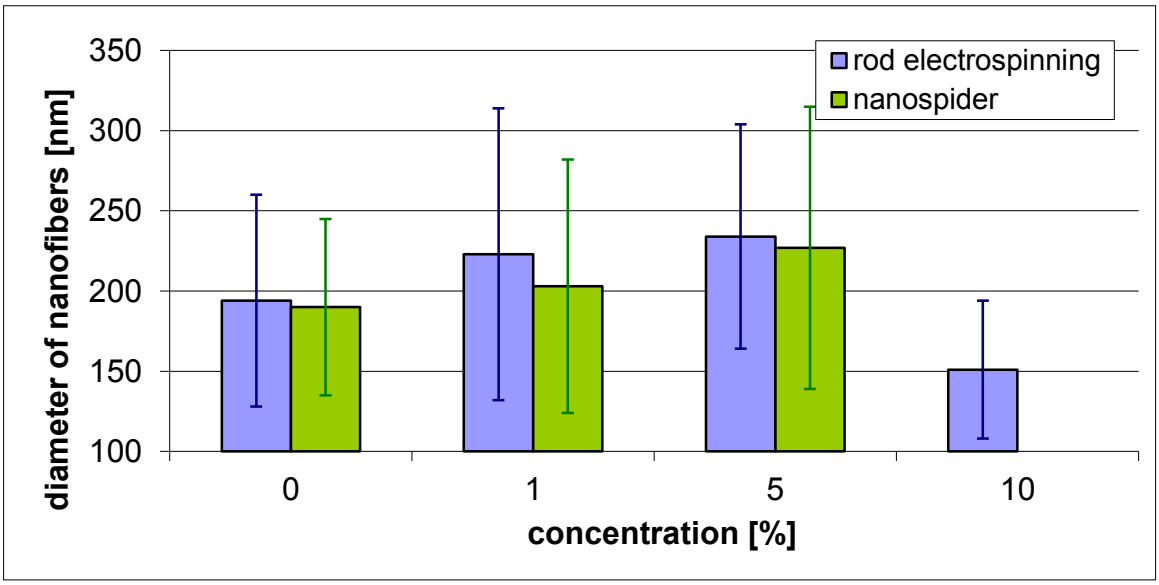


Figure 27: Graphs showing diameter of nanofibers from different techniques

Figure 26 shows the comparison of change in diameter with different techniques where C60 in PUR was electrospun with nanospider technology and C60Br in PUR was electrospun using rod electrospinning. The average diameters of C60Br in PUR are less when compared with C60 in PUR but both increasing as concentration increases. The SEM-EDS analysis is one of the techniques that can indicates the presence of C60 in PUR. Point analysis was used for PUR, blind sample and 1 wt% of C60Br because they show well whether the Br peak is visible or not then map analysis. There is so little difference between the two. The little peak appears of 1wt % of C60Br confirming at least there are few fullerenes inside nanofibers. Map analysis was used for 5 wt % and 10 wt % of C60Br because they show clearly that fullerenes are inside nanofibers and because they are not uniformly distributed, they form aggregates.

The Raman spectroscopy confirm the presence of C60 inside the nanofibrous layer, although the analysis also confirms that the distribution of fullerenes is still non-uniform (see figure 28). That is why a great willingness of fullerene to aggregate, thanks to their surface properties. The appearance of the peak at around ν = 1460 cm^{-} indicates the presence of fullerene C60.

There are additional peaks because C60 is polymerized through covalent bonding with neighboring molecules. There is a peak at about 3000cm^{-} indicating the PUR. Other low frequency peak appears in the Raman spectrum at about 500cm^{-}

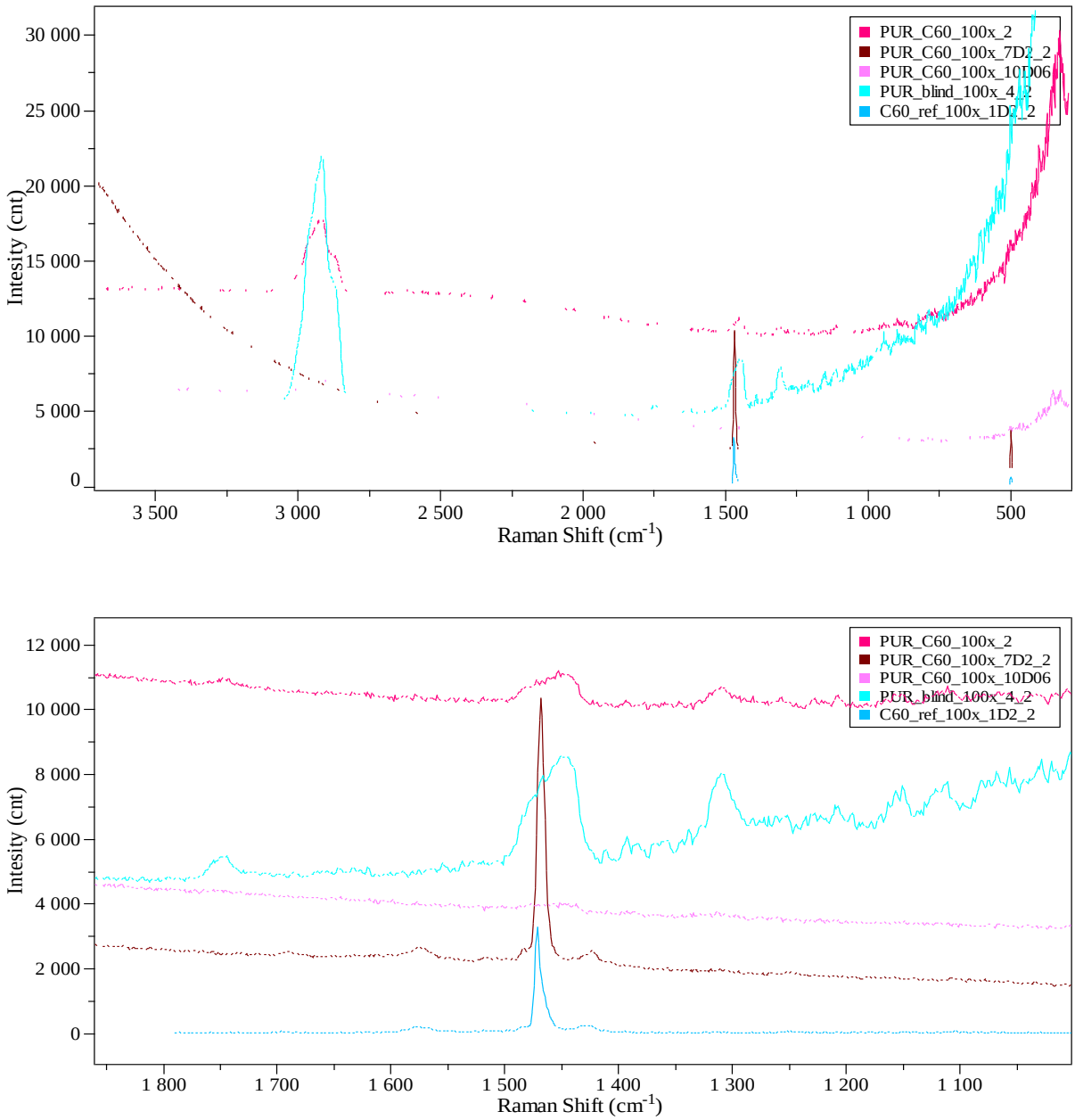


Figure 28: Two different Raman spectra with different resolution on axis x for pure C60 (powder), blind sample of PUR nanofibers and three different places of composite nanofibrous layer consisting of PUR with 1 wt% of C60.

The peak of pure C60 has low intensity compared to 1 wt % of C60 in PUR, because the concentration of C60 is low. The intensity is growing further signifying the presence of other polymerized C60 in the sample.

If comparing rod and cylinder electrospun nanofibers, there is no big variation of their standard deviations. Therefore the rod and cylinder electrospun in the same way meaning the parameters and conditions are nearly of the same standard. It also confirms the presence of fullerene because we can see from the table 1 that increasing C60 concentration in both techniques with the same amount resulted in increased in average fiber diameter with less variation. In both of them there is no pressure pushing the fibers into the collector except the electric field from applied voltage. High voltage of 60- 65kV was applied for cylinder because more solution in the bath of the rotating cylinder while it was 30-32 kV for rod electrospinning because of 1 bubble depending on the size of the bubble producing jet fibers to the collector. Cylinder is continuous and rod after all the solution is used or ejected from rod after few seconds stop the machine and put another one it is not continuous. This may affect the polymer nanofibrous material collected on the spun-bond material might get a thicker layer with less porosity, more fibers are randomly oriented or thinner layer with high porosity. High porosity will allow conduction of heat then the material will not be good for fire protection clothing.

It was difficult to electrospun 10wt% of C60 by rod electrospinning because of high viscosity and since there is no pressure pushing fibers to the collector like in syringe electrospinning, fibers fail to reach the collector only few jets of small sizes were able to electrospun from the bubble solution resulting in fall of average fiber diameter. Since could not be spun by only using the bubble from the rod then concluded that it would be possible to electrospun using cylinder. Equation 2 is applicable to needleless electrospinning up to certain level of loaded fillers unlike in needle electrospinning (depends on type of filler, solvent, polymer, etc.). High viscosity may affect the fiber morphology in needleless electrospinning. The velocity of moving spun-bond material (nonwoven) was 0.05m/min, the lowest velocity in order to prevent high porosity in the material. The disadvantage of rod electrospinning is time consumption.

Fiber diameter increases with solution viscosity based on the equation 2 shown below

$$d \propto \eta^{\alpha} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Viscosity increases with concentration based on the equation below

$$\eta \propto C^{\beta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The combination of equation 2 and 3 results in the following equation

$$d \propto C^{\delta} \quad \text{..... (4)}$$

Where $\alpha, \beta \; and \; \delta$ are scaling exponent and they are different for different polymers. The fiber morphology is getting worse as the concentration increases, more beads are formed due to agglomeration of fullerenes.

The study of the composite nanofibers with integrated spherical fullerenes leads to increasing of thermal resistance of such materials. This is why the TGA analysis was used for analyzing of selected samples. The selecting samples were of course blind sample of PUR and PUR nanofibers with 1 wt% of C60 from nanospider technology. The material had the smallest diameters of nanofibers and its production was easier than the others. The price of material is very important and lower amount of fullerenes means lowering of the total price. The results from TGA showed that composite nanofibers have significantly higher thermal resistance. The beginning of thermal decomposition shifted of 51°C (see table 3). The curves are characterizing the decomposition by endo-effect (PUR without C60) and by exo-effect (PUR with C60) as shown in (figure 29).

Table : Interpretation of the test results from PUR nanofibers produced by nanospider technology measurements

Nanofibers	*Temperature of the decomposition beginning [°C]*	*Δm/Δt [mg/min]*	*ΔH [kJ/kg]*
PUR (blind sample)	237	0.17	2625
PUR (1wt% of C60)	288	0.14	-2641

Δm/Δt – average rate of the sample weight loss
ΔH – thermal decomposition of color (ΔH < 0 exothermic reaction, ΔH > 0 endothermic reaction)

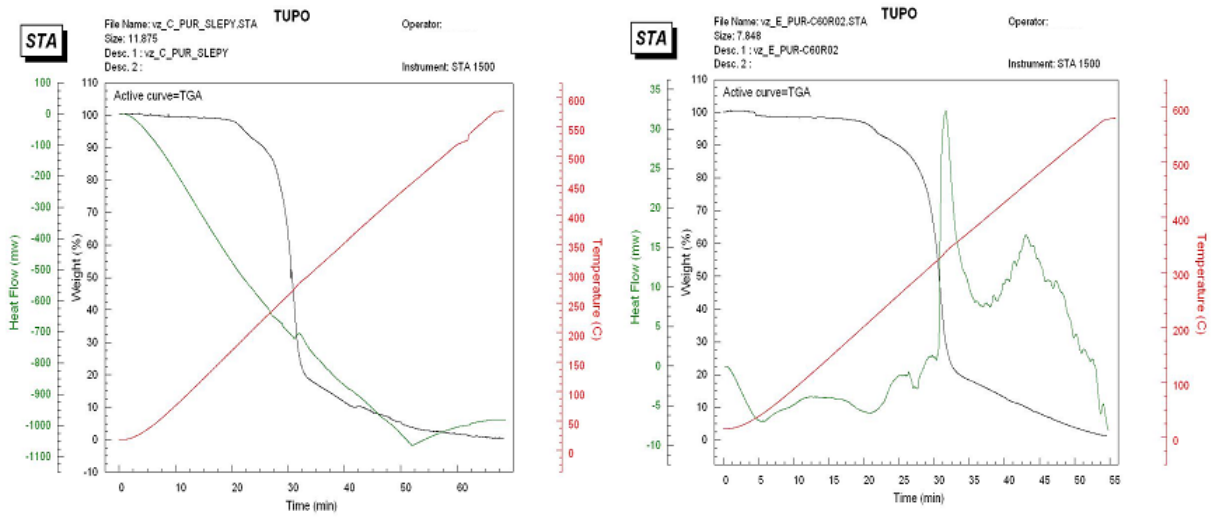
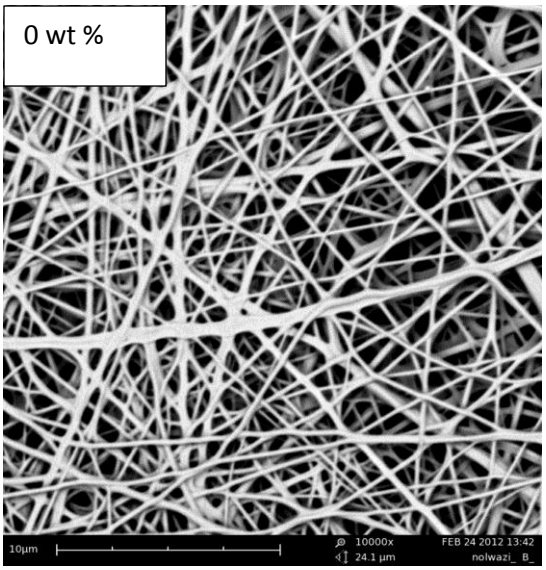


Figure 29: Thermal analysis graphs presenting blind sample of PUR nanofibers on the left side and PUR nanofibers with addition of C60 1 wt% produced by nanospider electrospinning technology.

6.2 Analysis of cross-linked PVA and non-cross-linked PVA with C60OH

Cross linking is used in polymers to promote a different in polymer's physical properties. Phosphoric acid and glyoxal were used as cross-linking agents for PVA as it is discussed in the experimental section (see chapter 1.2.2). The comparison of cross-linked PVA with C60-OH and virgin PVA with C60-OH are shown below by SEM images.


0 wt %
10µm
10000x
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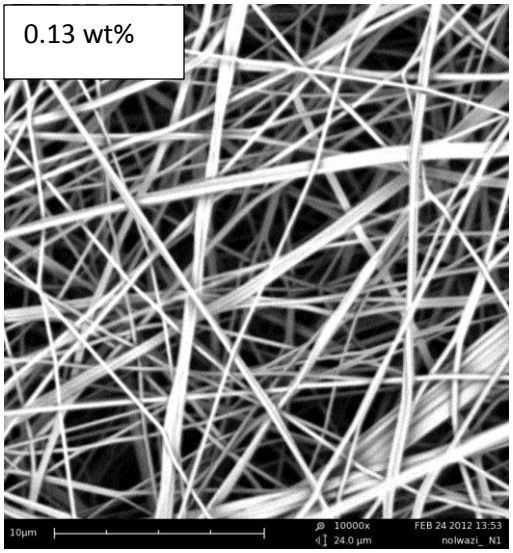
24.1 µm
nolwazi_ B_


0.13 wt%
10µm
10000x
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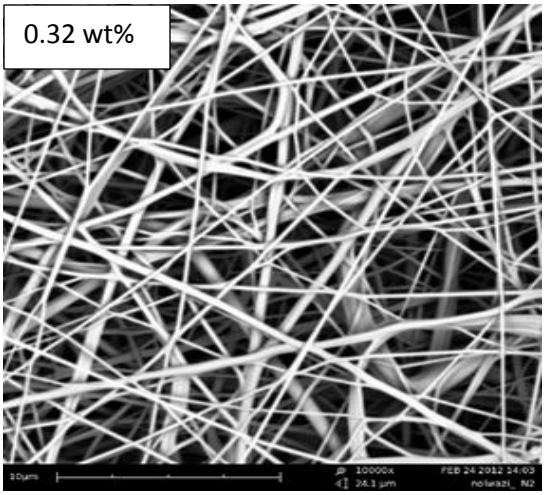
24.0 µm
nolwazi_ N1


0.32 wt%
10µm
10000x
FEB 24 2012 14:03
24.1 µm
nolwazi_ N2

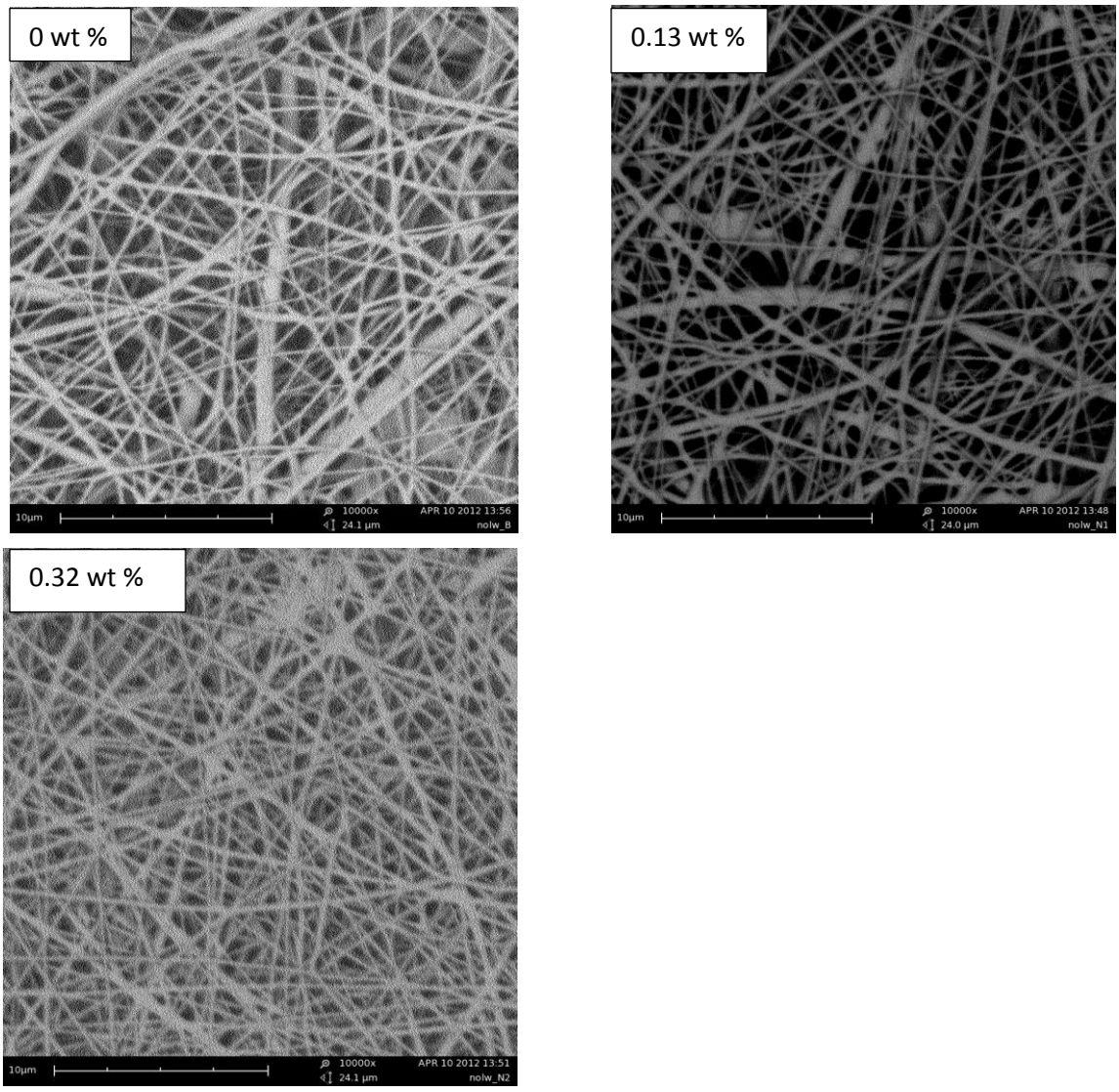


Figure 30: SEM images of PVA solution with & without crosslinking agents. The 1st 3 showing Solution without cross linking agents & the last 3 with agents present as concentration of C60-OH increases from 0, 0.13 to 0.32%. wt % of PVA.

The unmodified PVA showed distinct fibers compared to the heat treated (cross-linked) PVA. The present of cross-linking agents made the fiber morphology denser caused by the interlocking of chains resulting in a closed structure. The 4 wt % (of PVA) of phosphoric acid and 3 wt % (of PVA) of glyoxal were found to be optimum for crosslinking PVA. In the previous works with the PVA electrospinning at the Department of Nonwovens, Technical University of Liberec.

Table 4: Average fiber diameter measurements [nm] of PVA solutions

	Diameter [nm]	
C60-OH concentration [%]	non-crosslinked	crosslinked
0	207.00±55.93	210.14±56.40
0.13	215.69±71.85	213.95±72.74
0.32	222.19±93.23	219.35±73.85

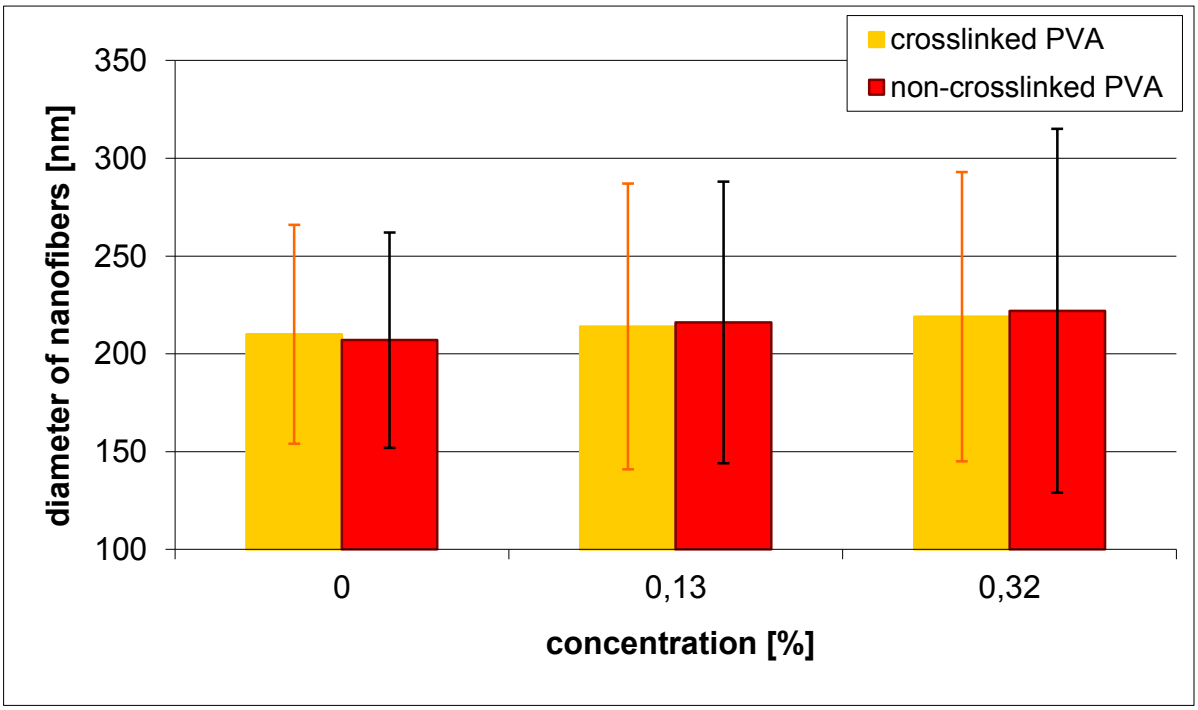


Figure 31: The nanofiber diameter with change in concentration of C60OH with and without agents

The Raman spectroscopy of PVA has many frequency peaks appearing (see appendix 2) because of hydrogen, carbon and oxygen molecules. The spectrum of 0.32 wt % of C60-OH shows a peak at about 1468 cm^{-} indicating that the sample is comprised of C60 and other frequency peaks indicate the PVA polymeric chains. The spectrum of 0.13 wt % of C60-OH has many frequency peaks appearing because of inhomogeneity of the solution as compared with 0.32 wt % of C60-OH.

Selected samples from set of samples were used for the TGA analysis. The PVA nanofibers as blind sample and PVA with C60-OH (0.32 wt%) were tested. The results, which are listed in table 5, showed that the samples with addition of C60oxi have significantly higher thermal resistance.

A change of thermal decomposition of nanofibers is evident from the curves of TGA (see figure 32) for nanofibers without and with the addition of C60oxi. The main exo-effect characterizing thermal decomposition of PVA blind sample is suppressed after the addition of C60oxi.

The beginning of thermal decomposition shifted to 90°C. The crosslinking of the PVA nanofibrous materials have a significant influence on thermal stability of final nanofibers.

Table 5: Thermal characteristics of nanofibers based on PVA with and without C60oxi

Material	*Temperature of the sample weight loss start [°C]*	*Temperature maximum peak of the first exo-effect [°C]*	*Thermal decomposition of color (the first exo-effect/total [mW]*
PVA-C60-OH (blind sample)	220	310	70/92
PVA-C60-OH (without crosslinking)	310	450	50/75
PVA-C60-OH (with crosslinking)	250	350	13/75

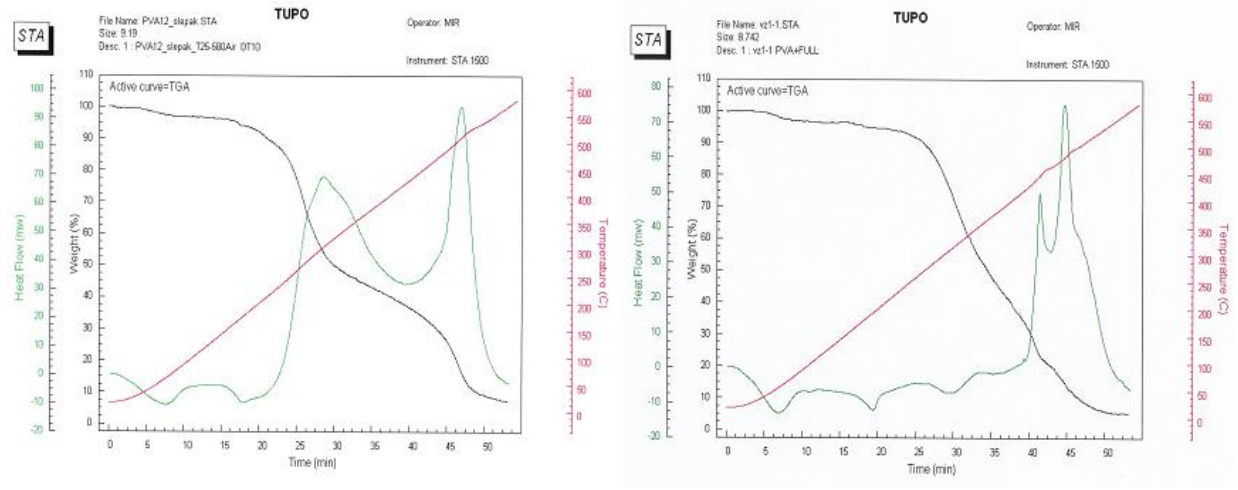


Figure 32: Thermal analysis graphs presenting blind sample of PVA nanofibers on left side and PVA nanofibers with addition of C60oxi.

The properties of polymer nanocomposites are governed by parameters including the dispersion of fullerene C60 and its interaction with these polymer matrices (PUR & PVA).

These parameters are influenced by the use of chemical treatments (OH and Br) at the filler's C60 surface. The use of fullerene C60 as nanofillers requires pre-treatment to improve the interaction between the filler and the matrix.

Raman Spectra (see appendix 2) gave a proof for the presence of C60 in the polymer nanofibers. The addition of fullerene C60 in polymers, the use of solvent and cross linking agents changed the properties of polymer solutions for electrospinning resulting in increased in average fiber diameters from SEM images. If fullerene was well dispersed within these polymers without the formation of aggregates would have enhanced better fire resistance properties by forming a compact and superficial layer that acts as a thermal barrier during the exposure to flames [23].

7. Conclusion

The fullerene C60 dispersed well in the polymer PVA but not so well in PUR, there were few formations of agglomerates from the observation of SEM images and Raman images. Formation of aggregates of C60 in polymers may be due to homogeneity in solutions formed by C60 aggregates. The defects in both polymer nanocomposites maybe resulted during electrospinning since there was no applied force or pressure like in needle electrospinning that forces fibers to jet with high speed and form less Taylor cones. It is difficult to electrospun polymers with fullerenes because no force that pushes fibers to the collector to form uniform structure. The heat treatment of PVA supposed to decrease the number of C60 aggregates in the PVA matrix because of the chemical reaction.

The presence of fullerene C60 can improve the thermal stability and flame retardancy of polymers even at low loading level proven by the results that were obtained from the EDS and TGA of C60oxi from the previous related worked table 3 [33] from the appendix. In comparison with other fillers including CNT, C60 took longer time to ignite resulting in burning resistance of the polymer thereby increasing thermal resistivity of the polymer. The fire behavior of the matrices was dependent upon the way the fillers were dispersed in the matrices. Fillers should be evenly dispersed to confer flame-retardant properties [23].

Raman Spectra also proved the presence of fullerenes inside polymer nanofibers with or without surface modification. The reason for using functional OH group for modification was to create polar bonds and hydrogen bonds between polymer PVA and fullerene C60 resulting in stability of the polymers. Polymer PUR reacted with C60 being modified with Br for better stability.

Fullerene C60 in polymer nanofibrous material can only be electrospun by needleless techniques up to 5 wt %. The fiber morphology of polymer nanocomposites and modification of interfaces are essential to maximize the properties [23]. The surface treatment and mixing are parts of key points that can dictate the performance of nanocomposites. The combination of nanofillers, matrix and additives allow wide possibilities of material by improving properties including mechanical, *thermal*, optical, and electrical as well as *reaction to fire*.

Future work should focus on which parameter to be improved during electrospinning and the spreading of C60 uniformly in the polymer matrix without the formation of aggregates in order to improve the polymer properties well so more research of this work still need to be done. The suggestion can be to use special surfactants for such application. The improvement on dispersion of fillers in polymer matrices and progress in production process can increase the range of application of such nanocomposites.

There were no analysis of the final chemical reaction between the polymer and fullerenes inside the nanofibrous layer. The analysis is of course necessary for better understanding of behavior of nanofibrous materials under different analysis. Thus it is also a suggestion for other research.

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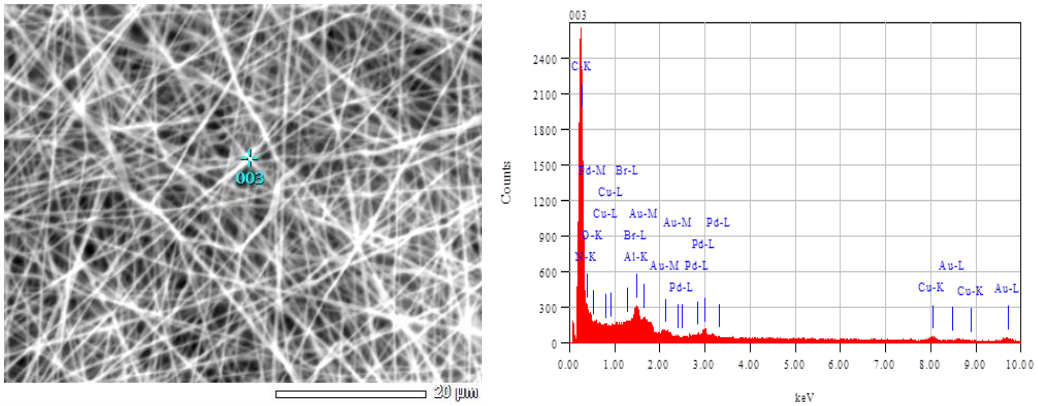
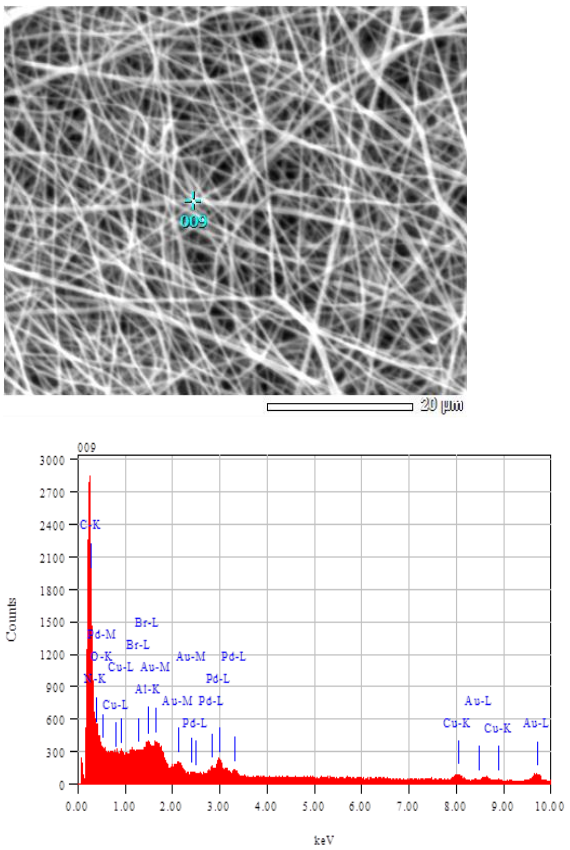
Appendix

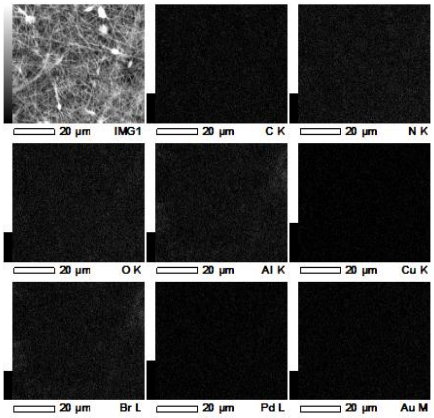
Appendix 1: SEM-EDS spectra with SEM images from which the spectra was done

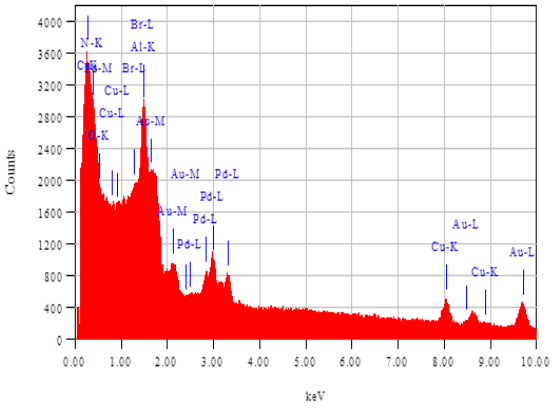


a) SEM-EDS point analysis of pure PUR nanofibers from rod electrospinning- no peak visible for Br.

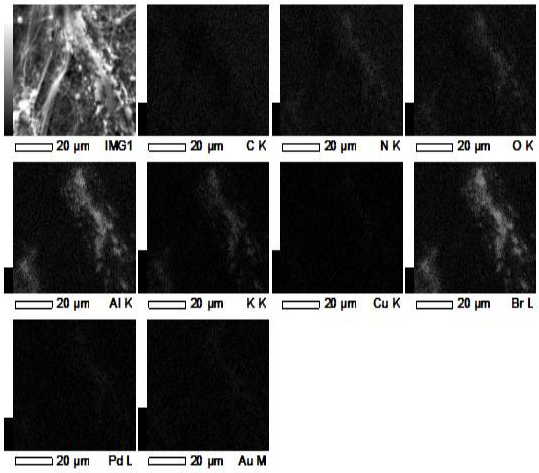


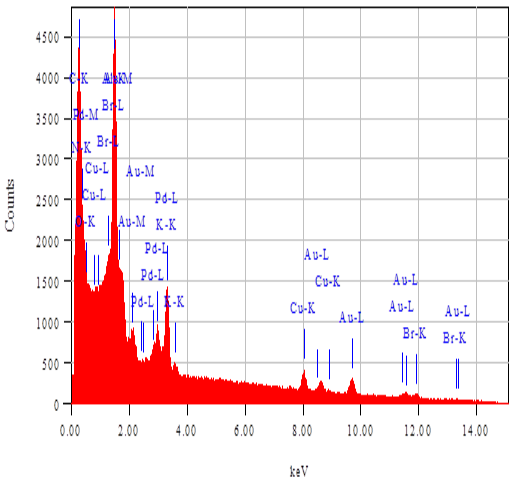
b) SEM-EDS point analysis of 1wt % of C60Br in PUR nanofibers from rod electrospinning – only a little peak presenting Br visibility.





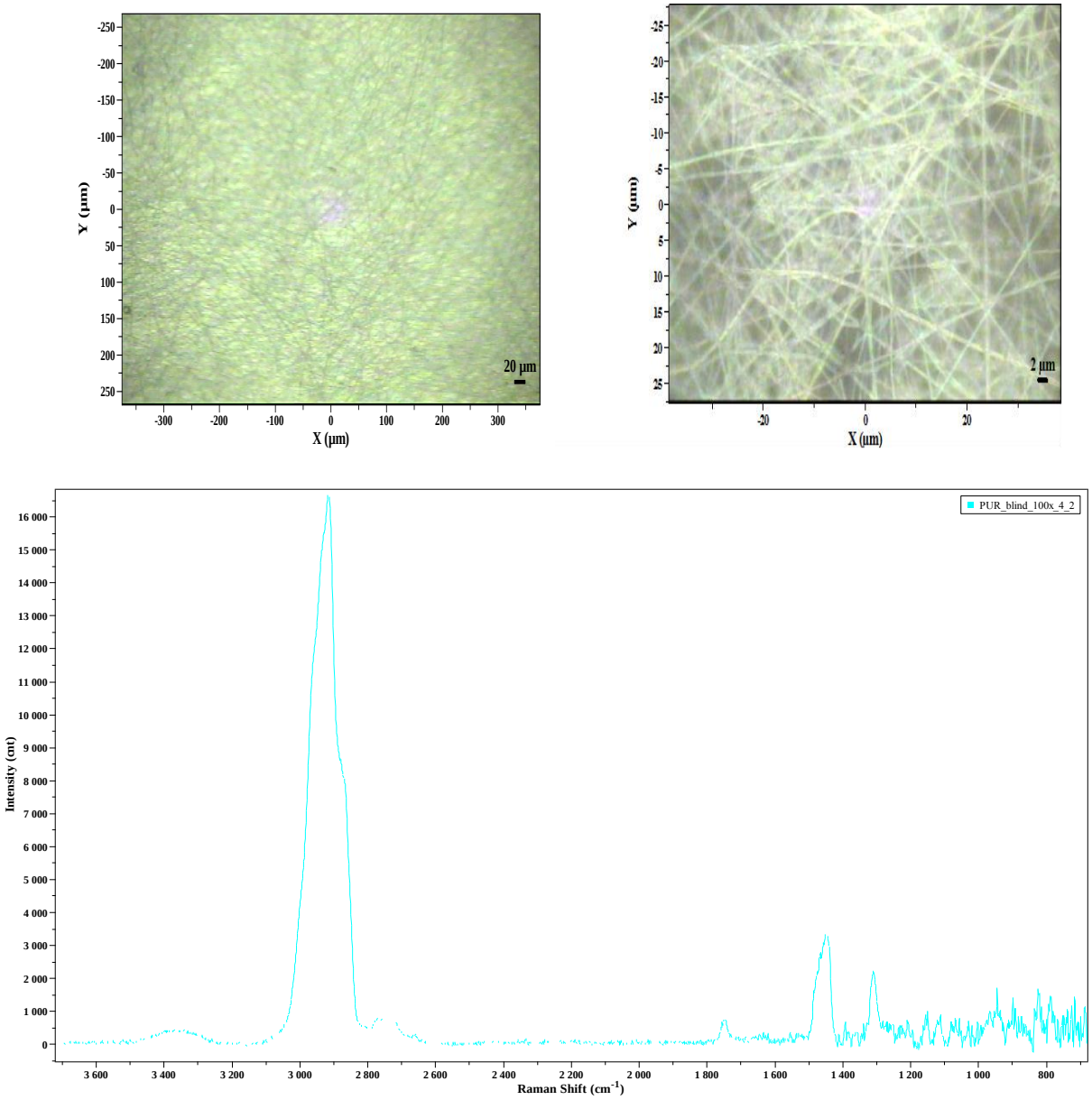
c) Map analysis of 5 wt% of C60Br in PUR nanofibers from rod electrospinning – significant peaks for Br are there.



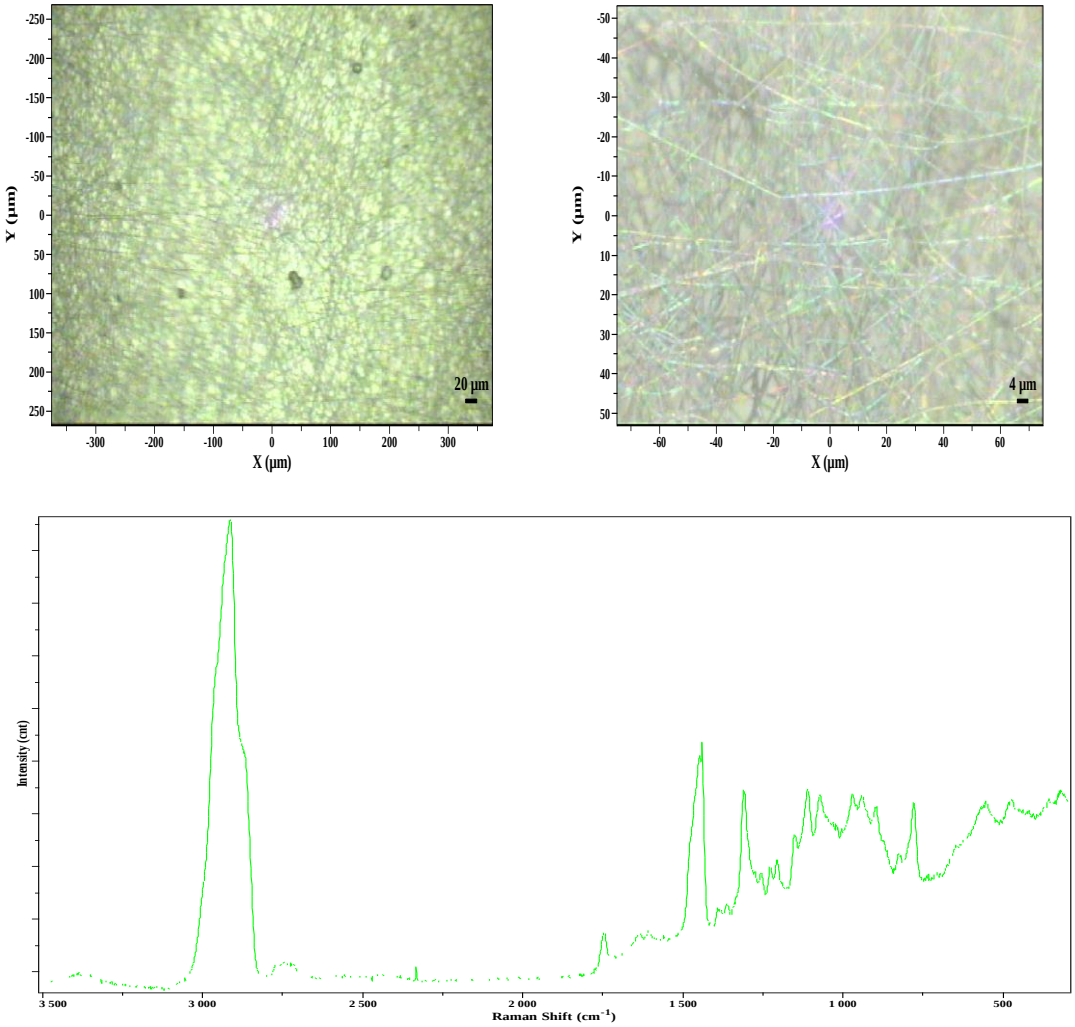


d) Map analysis of 10 wt % of C60Br in PUR nanofibers from rod electrospinning –significant peaks for Br are there.

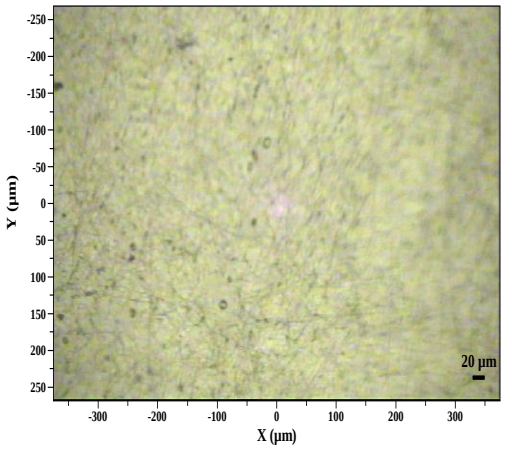
Appendix 2: Graphs from Raman spectroscopy and images from light microscope, which were used for analysis

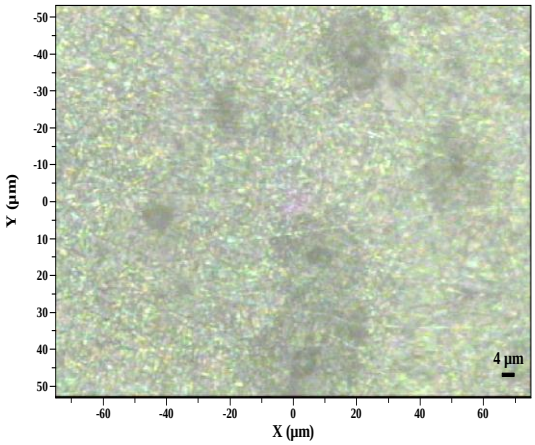


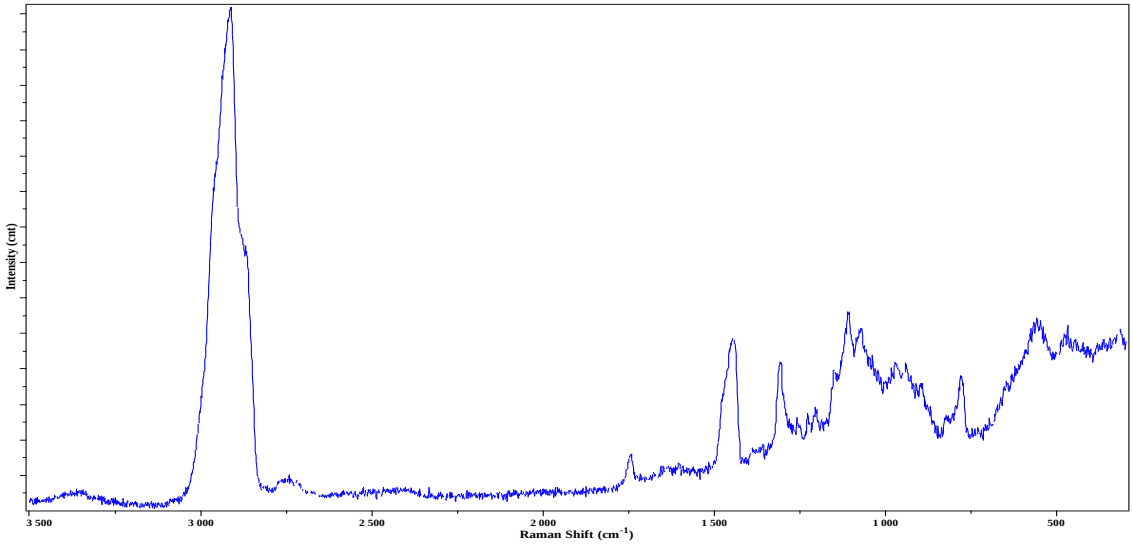
The Raman images and graph showing the presence of carbons of aromatics in PUR solution



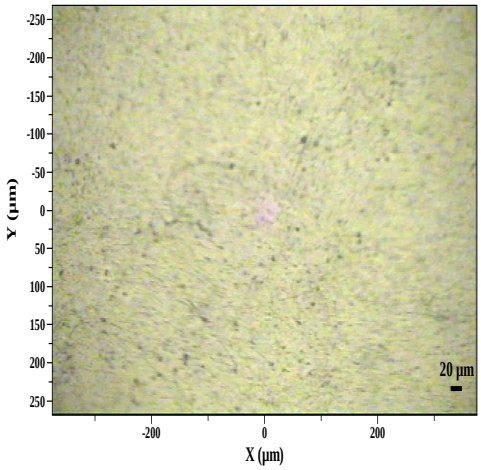
A Raman images and graph of PUR with 1 wt % of C60

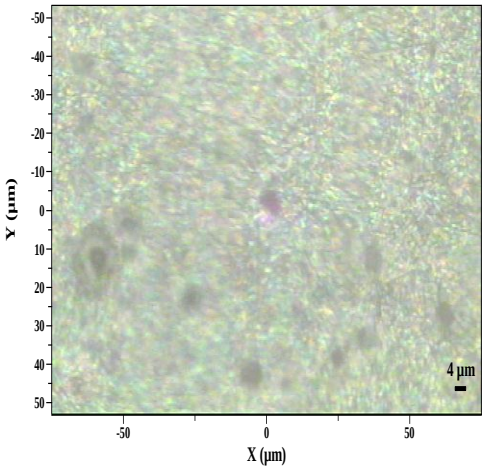


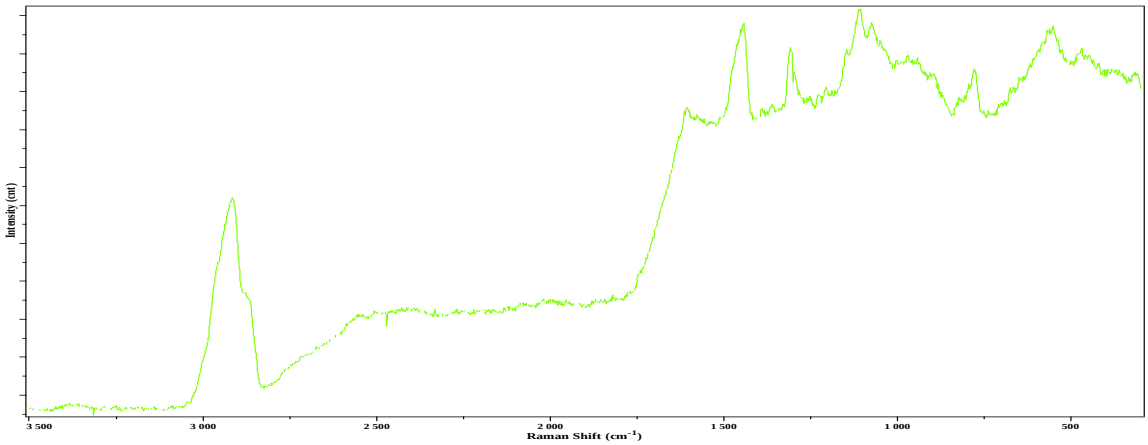




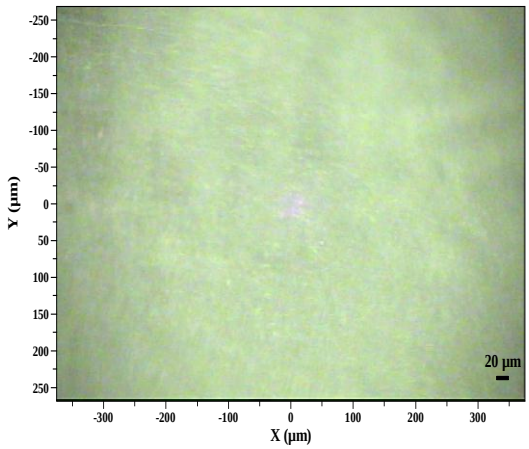
A Raman images and graph of PUR with 5 wt % $C60Br_{24}$

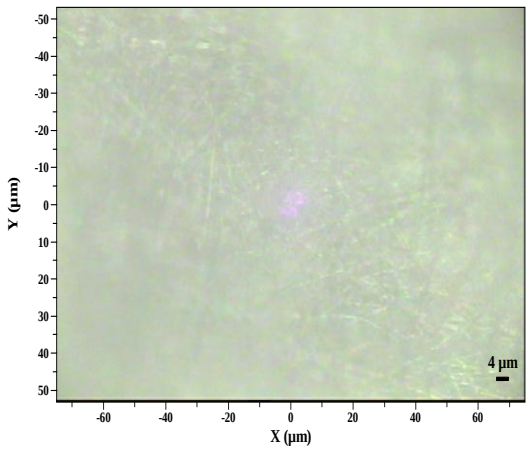


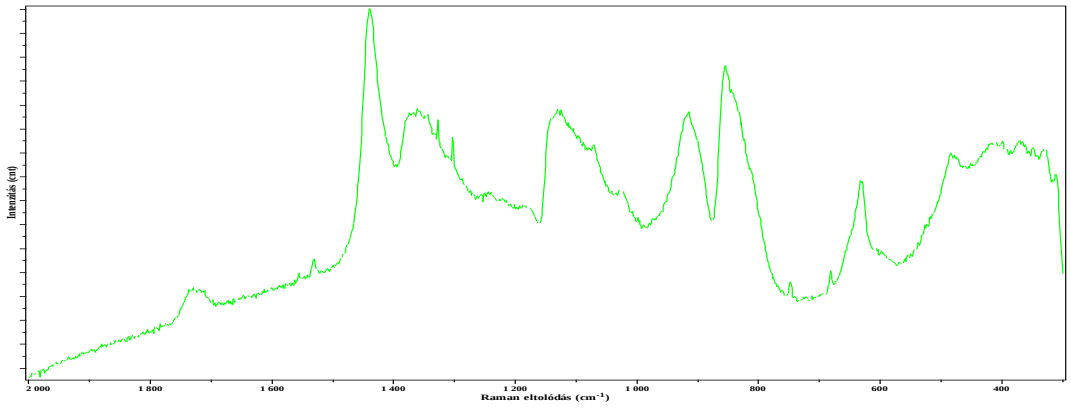




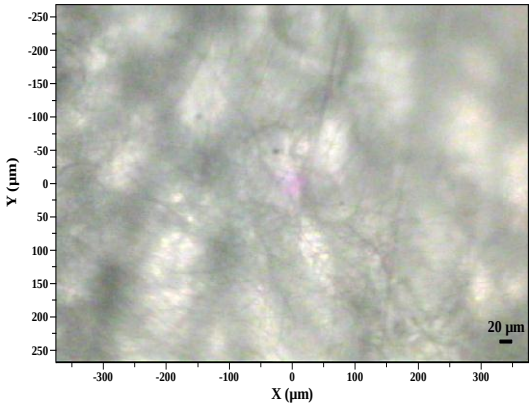
A Raman Images and spectrum graph of PUR with 10 wt % $C60Br_{24}$

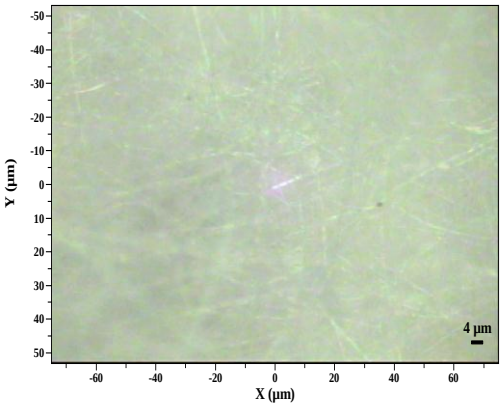


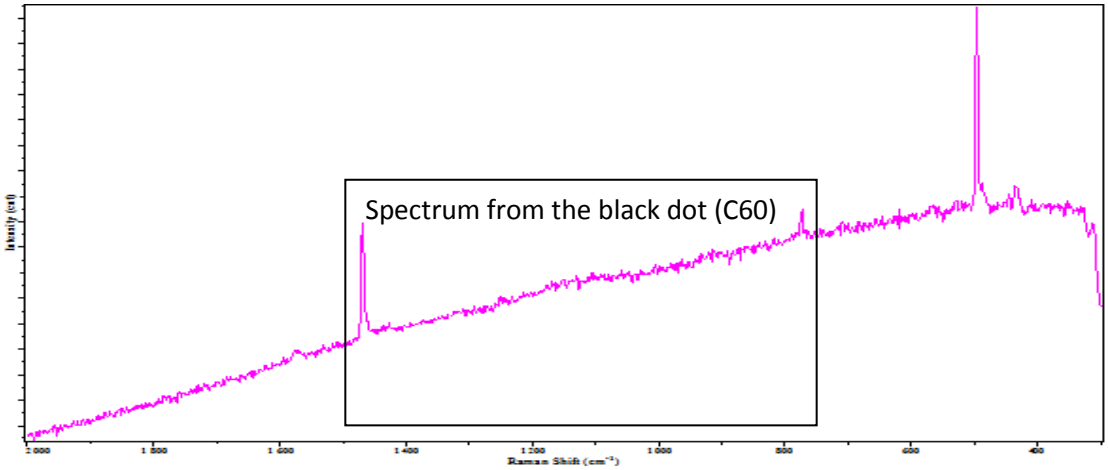




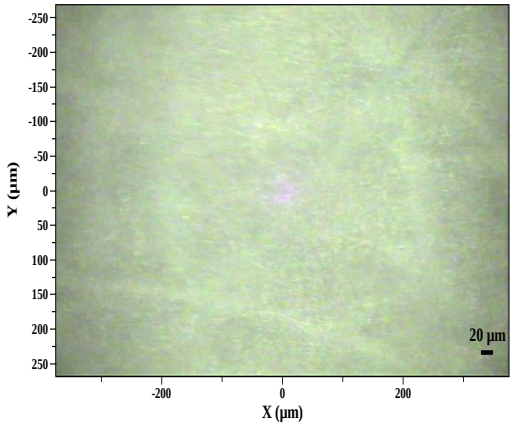
A Raman images and spectrum graph of non crosslinked PVA without fullerenes

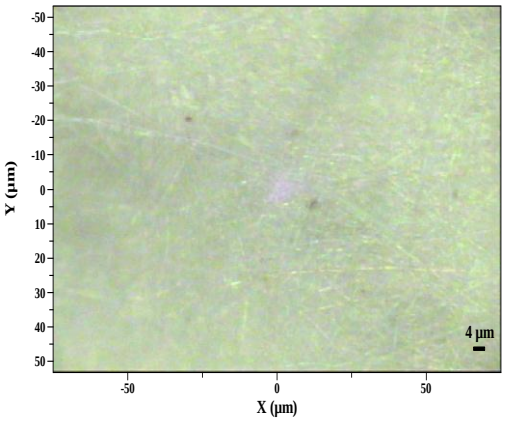


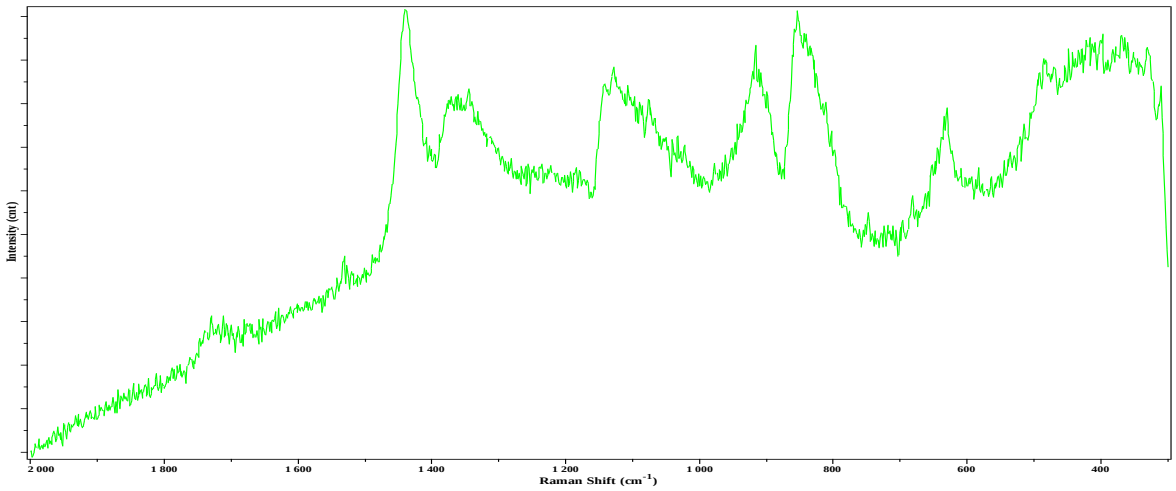




A Raman images and graph of non-crosslinked PVA with 0.32 wt % C60-OH


Y (µm)
X (µm)
20 µm


Y (µm)
X (µm)
4 µm



A Raman images and spectrum graph of non-crosslinked PVA with 0.13 wt % C60-OH